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INDUSTRIAL CHEMISTRY

A MANUAL FOR THE STUDENT AND MANUFACTURER

EDITED BY

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PREFACE

THE purpose in preparing this book has been to assemble the ideas of a large number of men who are recognized authorities in their respective lines and thus produce a volume which would represent modern American methods and processes. It has been the aim of the authors not to give undue attention to minor details in order that the student may more fully appreciate the fundamental principles set forth. The subject matter is essentially descriptive without, however, omitting the theoretical considerations necessary for the proper understanding of the subject.

The editors ask the indulgence of the reader for any errors or omissions that occur in the present volume. In a work of this character, covering so wide a range, frequent revisions will be necessary, and they will be grateful for any suggestions with this end in view that may be submitted to them.

The authors' acknowledgments are due to the various manufacturers who have furnished cuts of their machinery; to Mr. George C. Abbe for his aid in the preparation of drawings; and to Mr. Charles M. Allen, who has given valuable assistance in the preparation of the manuscript.

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INDUSTRIAL CHEMISTRY

I

GENERAL PROCESSES

A. B. AUBERT AND ALLEN ROGERS

Grinding. One of the most important operations which we encounter in chemical industry is that of grinding. Not only must the raw material be reduced to a state of fine division before it can be used, but the finished product, in many instances, must be placed on the market in the form of a fine powder or paste. The results to be secured depend entirely upon the nature of the material and the purpose for which it is to be employed. There are two general divisions, however, of grinding machines: those which are used for crushing and coarse grinding, and those which produce a fine powder.

Jaw Crusher. The simplest and least expensive form of crusher in use is that known as the jaw crusher,[1] Fig. 1. It consists of a station-

Fig. 1.

ary steel plate against which a corresponding steel jaw works on a cam, thus giving a rolling motion. This form of machine is capable of crushing the hardest of materials. The working parts may be regulated by means of an adjusting screw, so as to give a coarse or fine product as desired.

[1] Sturtevant Mill Co., Boston, Mass.

Crushing Rolls.[1] This type of machine is employed quite extensively for reducing the product of the jaw crusher to a finer state of division, or for soft materials. Its construction is well illustrated in Fig. 2, which consists of two plain or corrugated rolls held on a firm foundation. The cover opens as shown, and carries the side plates and hopper, thus making the parts easily accessible for cleaning.

Rotary Fine Crusher.[1] For rocks of moderate hardness the rotary crushers are almost universally used. These machines are provided with

Fig. 2.

double doors that carry all of the grinding parts, and swing open as easily as the doors of a safe, thus at once exposing every part to inspection. They are built with capacities of from 2 to 30 tons per hour. They may be regulated, while running, for fine or coarse work by turning the adjusting wheel, Fig. 3.

Disintegrator.[2] This type of machine, also known as pulverizing mill, is especially adapted for such materials as are of a lumpy nature, such as dry colors, soft pigments, borax, sulphur, starch, etc.; also for mixing dry materials, such as fertilizers, for example. The construction

[1] Sturtevant Mill Co., Boston, Mass. [2] Chas. Ross & Son, Brooklyn, N. Y.

of this machine is very simple, as will be seen from Fig. 4 and 5. The steel cages run at a very high speed in opposite directions, thus driving the material through the steel bars by centrifugal force, and pounding it to

Fig. 3.

a powder. They are very strongly built; and may be very easily and quickly cleaned by taking off the top half of the casing, removing the bolts holding bearing frames to bed plate, then drawing frame and cages apart by tail screw, as shown in the illustration.

Fig. 4.

Chaser.[1] There are many materials which, owing to their peculiar nature, cannot be crushed by means of the machines described above. Such substances as seeds and drugs are best powdered by means of the chaser. It is also employed in mixing loams for use in foundries, for mix-

[1] Chas. Ross & Son, Brooklyn, N. Y.

ing mortar, and for mixing and crushing in a semi-dry state. The chaser, Fig. 6, is constructed with a stone or steel bed on which rotates one or two "edge runners" or "travelers." The travelers are driven by a vertical shaft, which is made of proper length to suit the height of the ceiling or room in which it is set. An arm provided with a scraper travels just in front of the runners, which brings the material under the heavy rollers, while the whole is set in a pan arranged with a gate for discharging.

Burr Stone Mills.[1] For fine grinding of dry or wet materials stone mills are most commonly employed, and are exceedingly well adapted for the purpose. Figs. 7 and 8 show the horizontal burr stone mill and the under-driven dry mill. Each form is provided with a hopper into

Fig. 5.—(open).

which the crushed material is fed, where it is transferred by centrifugal force to the effective parts of the stone. Fig. 9 shows a rational arrangement for crushing, grinding and packing of dry materials. Many mills are provided with cooling arrangements to prevent the excessive generation of heat. This is especially necessary in the grinding of paste colors or paints, and is well illustrated in Fig. 10, which shows the Ross Improved Paint and Color Mill as ready for work.

Ball Mills.[1] There are various types of these mills on the market. That shown in Fig. 11, consists of a cylinder of cast iron having an opening on the side through which is placed the charge. The door covering this opening is dust-tight and is held in position by means of two steel clamp nuts. Inside of the cylinder is a large iron ball which rotates when the cylinders are revolved, and by means of which the grinding or pulverizing is done. The pulverized material is all retained in the cylinder, therefore nothing is lost by the floating away of dust.

[1] Chas. Ross & Son, Brooklyn, N Y

Pebble Mills.[1] Pebble mills grind principally by friction, the effect being produced by the sliding, tumbling and rolling inside of the mill of a great number of flint pebbles or porcelain balls which are mixed with the substance to be ground, and the movement being caused by revolving the mill at a regulated speed. As pebble mills are not crushers, all material

Fig. 6.

should be crushed to a certain degree of fineness before being charged into the machine. The mill shown in Fig. 12 is lined with vitrified porcelain, thus presenting a grinding surface which will neither contaminate nor discolor the material being pulverized.

Tube Mills.[1] The general principle of grinding employed by the tube mill is the same as in the ordinary pebble mill, the difference being that

[1] Abbé Engineering Co., New York City

Fig. 7.

Fig. 8.

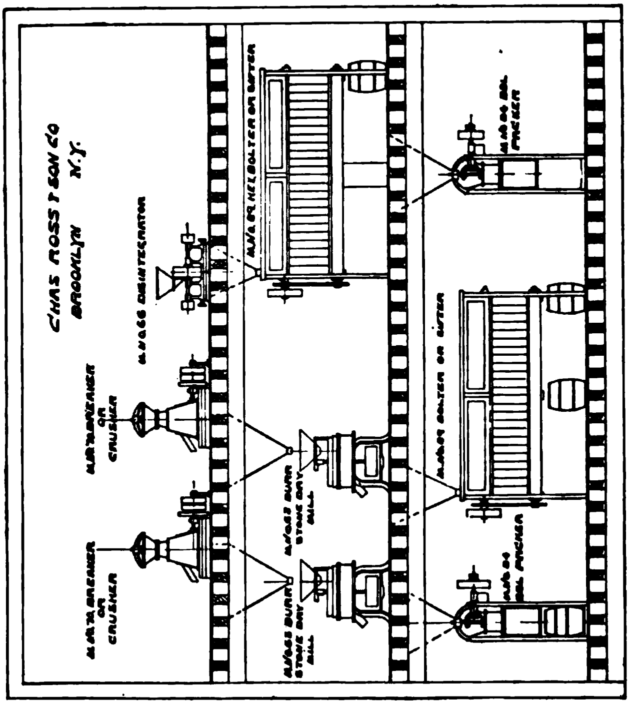

FIG. 9b.—Arrangement for Crushing, Grinding, Sifting and Packing.

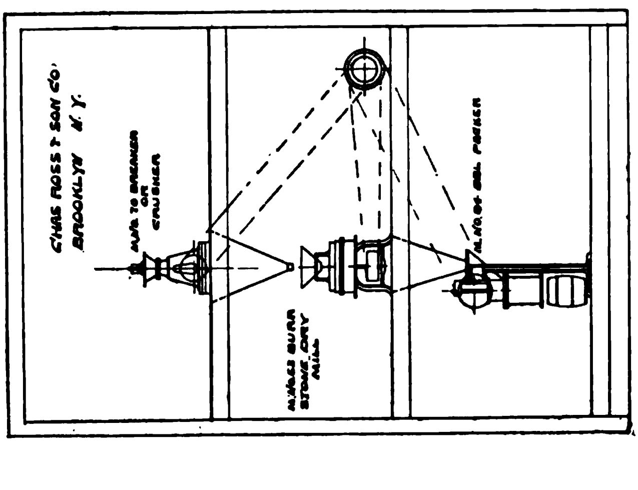

FIG. 9a.—Arrangement for Crushing, Grinding and Packing.

Fig. 10.

Fig. 11.

the material to be ground in the tube mill is fed in at one end and is delivered as a finished product at the other, the fineness of the product being regulated simply by the speed at which the material is fed into the machine. The slower the feeding the longer the material receives the action of the pebbles and the finer the discharged product will be. To make a coarse material the feeding is increased. Fig. 13 shows the Abbè Tire Style of tube mill, 4 ft. 6 in. in diameter by 20 ft. long.

Some of the more modern forms of tube mills are provided with a "Spiral Feed," Fig. 14. By means of a crescent-shaped opening located where the spiral starts, a certain quantity of the material is allowed to enter, and as the machine revolves this travels forward until it reaches the center, where it enters the grinding chamber. Thus after two or three revolutions there is a constant feed of a regular amount of material.

Fig. 12.

From the grinding chamber the product passes through a perforated plate into a reverse spiral and thence discharged from the center of the machine. In this way all labor of shoveling pebbles is avoided.

Roller Mills.[1] For the grinding of lithographic inks, colors in varnish, chocolate and many other pasty materials the above methods cannot be satisfactorily employed. The roller mill obviates the difficulties encountered and is largely used for the purposes mentioned. In their construction these machines usually consist of three steel rolls, which rotate at different speeds, thus passing the product to the front, where it is detached by means of a scraper, and falls onto the apron. By means of adjusting wheels the front and back rolls are under perfect control, and may be set to any degree of fineness desired. Fig. 15.

Sifting.[1] In those instances where the substance being treated is ground in a dry condition, it is often necessary to separate the coarse from the fine material. This is accomplished by the use of sifting or

[1] Chas. Ross & Son, Brooklyn, N. Y.

Fig. 13.

bolting machines, there being numerous forms and styles employed for the purpose. The degree of fineness is regulated by using either wire sieves or bolting cloth. In all cases the ground material enters the reel,

FIG. 14.—Spiral Feed.

and as this rotates the fine powder passes through the meshes, leaving the coarse particles in the reel. See illustration, Fig. 16.

Sedimentation. In order to overcome the annoyance and loss caused by flying dust, many materials are ground in water. As the resulting

FIG. 15.

turbid liquid comes from the mill it is allowed to flow into the first of a series of tanks, where the coarser and heavier particles rapidly subside, leaving the finer substance in suspension. The liquid is then drawn to

the second tank, where it is allowed to remain somewhat longer than in the first tank. In each of the subsequent tanks the liquid is allowed to remain for a longer period than in the one previous, thus giving various degrees of fineness to the resulting product, the coarse particles being

Fig. 16.

returned to the mill for further grinding. This operation is sometimes spoken of as "levigation."

Filtration. By this process is meant the separation of suspended solids from a liquid, and often presents grave difficulties; especially is this so when working with large volumes. The medium employed may

be paper, cloth, cotton, wool, asbestos, slag or glass-wool, unglazed earthenware, sand or other porous material.

Ribbed Filter. For handling small amounts of material the ribbed filter is very convenient, and consists in folding an ordinary large filter in such a manner that when inserted into the funnel it will leave canals along the side. To prevent breaking of the filter the tip should be forced well into the neck of the funnel.

Bag Filter. A very satisfactory method of filtering coarse material is to arrange four pieces of wood as shown in Fig. 17, and on the brads suspend a piece of muslin in such a manner as to form a bag. The portion passing through at first may be slightly cloudy, but as the pores fill with the precipitate the filtrate becomes clear.

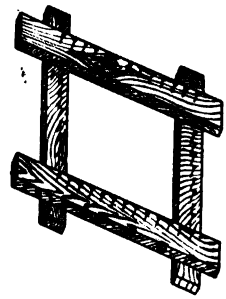

FIG. 17.

Suction Filter. This form of filter is used very largely where it is desired to retain the filtrate as well as the solid matter. It consists of a box arranged so that the lower section is connected with the vacuum pump, and over the perforated bottom is placed the canvas or other filtering medium.

Filter Press.[1] A very rapid and convenient method of filtration is by means of the filter press. Although they are all built on the same principle, their details of construction vary to a marked degree. In its simplest form, however, it consists of distance frames and plates. These plates and frames rest upon a pair of parallel bars, and are held in position by means of lugs projecting from each side. Over the surface of each plate is stretched a filtering medium, usually cloth, which is held in place by means of pegs; the whole being forced against the adjacent frame by means of a screw or hydraulic pressure. The material to be filtered is forced through the channel along the top of the press and into the distance frames. The solid material is held back by the filtering medium, gradually filling the chambers and producing a solid cake. The liquid which passes through the filter is allowed to discharge into the channels along the lower portion of the press, where it may be recovered or discarded as wished. A standard press is shown in Fig. 18.

Centrifugal Machine.[2] This appliance is used for separating liquids from solids. It is especially adapted to the drying of crystals in that it throws off the adhering mother liquor by centrifugal force. It is also employed for drying yarns, textiles, wood pulp, sugar, starch, etc. The centrifuge, therefore, is used more as a means of drying than of filtration. It consists of a cylindrical perforated basket fixed to a vertical shaft, which rotates at a very high speed (900 to 1200 revolutions per minute), Fig. 19. By means of the centrifugal force generated the contents of the basket is

[1] T. Shriver & Co., Harrison, N. J. [2] American Tool and Machine Co., Boston, Mass.

Fig. 18.

driven to the outer wall, where the solid material is detained, and the liquid thrown off. In working with the machine great care must be exercised lest grave accidents occur. It is also necessary to see that the machine is carefully constructed.

Drying. Before submitting material to the drying process proper it may be advantageous to remove as much of the adhering liquid as possible by draining, filtering, or centrifuging. The water that still adheres is now removed by evaporation in contact with the air at as high a temperature as compatible with the substance and economical practice. Whenever waste heat is available it should be used.

FIG. 19.

In order that drying should be uniform the substance to be dried is stirred, usually by mechanical appliances. The simplest arrangement would consist of a platform of metal or stoneware heated by flue gases and upon which the material would be spread and stirred from time to time; this is not, however, an economical process. A less wasteful method is by the use of drying chambers, built of brick, wood, or metal. The chamber may be heated from the inside, or the air passing through it may be heated. To aid in the removal of the moist air an exhaust or fan is usually employed.

Where temperatures of 100° C. or less are desired the air may be heated by passing it over steam-heated coils, or the plate on which the

material is placed may have a steam-heated jacket. As the point at which the heat enters the apparatus, be it steam or flue gases, is the point of greatest heat, it is usual to provide for the conveying of the material from the further and cold end of the apparatus toward the hottest portion. For this purpose the shaft furnace can be used, provided the material is hard enough and there is no need of regulating the temperature very carefully. A large number of more or less efficient forms of dryers are manufactured, among which vacuum dryers, in which the drying is done at a considerable saving of labor, fuel and time, are the most important. Vacuum dryers[1] may be divided into shelf dryers, Fig. 20, for material that does not need to be stirred while drying; rotary dryers for

FIG. 20.—Vacuum Shelf Drier.

material which must be continuously stirred; and drum dryers for substances like glue, which readily forms a dry film on the surface.

Lixiviation. The process of lixiviation consists in the separation of water-soluble material from insoluble or less soluble material. The substance to be treated with water may be suspended in bags or baskets, or placed in tanks provided with perforated false bottom. The solution, being denser than water, sinks to the bottom and may be removed. The material is usually submitted to a systematic treatment with water, in such a manner that the pure water first comes in contact with the nearly exhausted substance, and then with the less exhausted in another tank, and so on until it reaches the last tank containing the fresh material.

[1] J. P Devine Co., Buffalo, N Y.

Such a series of tanks is known as a battery. The term *extraction* is generally used when solvents other than water are employed. It is possible to extract several substances from the original raw material by the successive use of several solvents such as water, alcohol, ether, and naphtha.

Crystallization. Crystals are geometric solids which may form by the separation of a compound from its concentrated solution. The solubility of most substances increases as the temperature of the solvent, usually water, is raised. A limit may be reached, however, for every temperature when no more will dissolve, and the solution is said to be saturated. If the temperature be now decreased crystals of the substance will separate; and these crystals, though formed in an impure mother liquor, may be quite pure. By evaporation or concentration of the mother liquor more crystals will result; which, however, will be less pure than the first crop. Thus this operation may be continued until the impurities accumulating in the liquor become so great that the crystals will enclose a large amount of foreign matter. This difficulty can be prevented to a certain extent by stirring the solution while crystallization takes place; this causes the separation of very small crystals, or crystal meal, which can then be washed so as to remove the adherent impurities.

Fractional Crystallization. Crystals may be further purified by several successive recrystallizations. This is a method used for the separation of substances when mixed in a solution; isomorphous substances, that is, those crystallizing in the same system cannot, however, be separated in this manner. The only way to proceed in such a case is to so react upon the solution as to change the chemical composition of one of the substances in such a manner that separation by crystallization becomes possible. As an instance of this may be mentioned the preparation of pure copper sulphate from a mixed solution of copper and ferrous sulphates. When blue vitriol is made from copper pyrites it is usually accompanied by more or less green vitriol. From this mixed solution only crystals of copper sulphate mixed with iron sulphate can be obtained, these salts being isomorphous. By oxidizing the ferrous to the ferric sulphate this may be avoided and pure copper sulphate prepared.

Calcination. In the process of calcination substances are submitted to the action of high heat, but not, however, to the point of fusion. Material may be calcined: to drive off moisture, to drive off some volatile constituent or cause a chemical action such as oxidation or reduction. The terms *roasting*, *firing*, *glowing* or *burning* are sometimes used in place of calcination. The process is usually carried on in furnaces, of which there are three common types: *reverberatory*, *muffle*, and *kiln*.

Reverberatory Furnace. In the reverberatory or open roaster the material to be heated is exposed to the direct action of the fire gases. It consists essentially of an arched chamber built of brick and heated from a grate placed at one end, while the products of combustion and

reaction are removed by a chimney at the other end. The material is placed upon the bed of the furnace, the fire gases pass over it and are deflected by the arched form of the roof of the furnace so as to come more directly in contact with the charge. The inside of such furnaces are lined with firebricks, while the outside are built of common bricks.

If an oxidizing reaction is desired, that is, if the fire gases are to contain an excess of oxygen, such conditions may be produced by setting the fire bars widely apart and feeding the fuel in thin layers at a time. Should a reducing action be desired the fire bars must be placed closer together and the fuel charged in thick layers.

Muffle Furnace. The muffle furnace, closed or blind roaster is built in such a manner that the fire gases do not come in contact with the substances to be calcined. It generally consists of a muffle of firebrick with the flues so arranged that the hot gases pass underneath the bed of the muffle and are then conducted over the top back to some point near the grate, where they are discharged into the chimney. A pipe is sometimes fitted to the top of the muffle in order to discharge any gases which may be formed during calcination.

Revolving Furnace. It is frequently necessary to stir the material during calcination, which would entail much heavy labor if done by hand; to obviate this, mechanical means have been devised, the most important of which is the revolver or revolving furnace. It consists of a drum or cylinder of iron or steel, Fig. 21, lined with refractory material and open at both

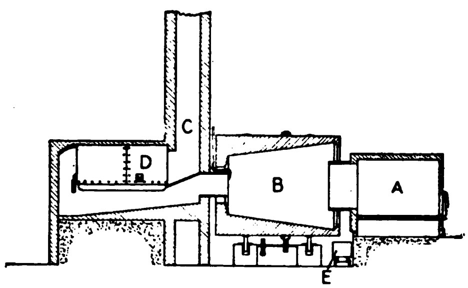

Fig. 21.—Revolving Furnace.

ends. The drum, which may or may not be inclined, revolves slowly about its longitudinal axis, while the highly heated gases, from the grate situated at one end, pass through it. The hot gases leaving any of these furnaces may be economically used for drying or evaporating.

Kilns. Kilns or shaft furnaces may be periodic or continuous, and are very largely used in the burning or calcination of limestone. In periodic kilns the calcined charge is allowed to cool, then withdrawn and the kiln recharged with fresh material. In the continuous form the calcined material is drawn from the bottom at the same time that a fresh charge enters the top, the operation being a continuous one.

Evaporation. By evaporation is understood the conversion of a liquid into a vapor for the purpose of recovering any solid matter which may be dissolved in it. In most instances the liquid to be evaporated is water, as other liquids would be recovered, and the process would be termed *distillation*.

Spontaneous Evaporation. This method is usually conducted in the open air by exposing the liquid in large shallow pans. The time required depends entirely upon atmospheric conditions, the best results being obtained on a windy day in hot, dry weather.

Evaporation by Direct Heat. By this method the flames or hot gases may play directly on the bottom of the containing vessel, or they may be made to pass over the surface of the liquid. In the former case, Fig. 22, the usual method is to employ large shallow pans which are so

FIG. 22.—Bottom Heated Furnace.

arranged as to be heated from the waste gases from other operations. In the latter mode of evaporation, Fig. 23, the flue dust and ashes are very apt to fall into the pan, thus causing the product to become impure. This method is used, however, to some extent where the purity of the product is not essential.

Evaporation by Indirect Heat. The use of steam is very largely employed for the reason that it is convenient to handle, and there is no danger of injury to the product by overheating. The simplest means of utilizing this method of heating is to circulate the steam through coils of pipe arranged inside the vessel. This method is especially adapted to the heating of liquids contained in wooden tanks. The temperature to which the liquid may be raised depends wholly upon the steam pressure, which may be regulated to suit the conditions required.

Steam-jacketed Kettles. The most convenient method of applying steam is by means of the steam-jacketed kettle, a cut of which is shown in Fig. 24. In conducting an evaporation the valve to drain pipe is opened in order to allow the first condensations to escape, and to prevent bumping. The exhaust valve is now opened, the inlet valve given a half turn, and then slowly opened until a good supply of dry steam issues from the drip. The drip is finally closed and the inlet of steam so regulated

as to secure the proper heat for evaporation The kettles in common use are constructed of copper or cast iron, the jacket usually covering one-half of the kettle. For purposes where copper or iron would not resist the action of acids or other chemicals it is customary to employ an enameled

FIG. 23.—Top Evaporation.

lined kettle, which enamel consists of an easily fusible glass. In many operations it is necessary to stir the liquid being evaporated, to accomplish which the kettle is generally equipped with an agitator provided with paddles of various shapes.

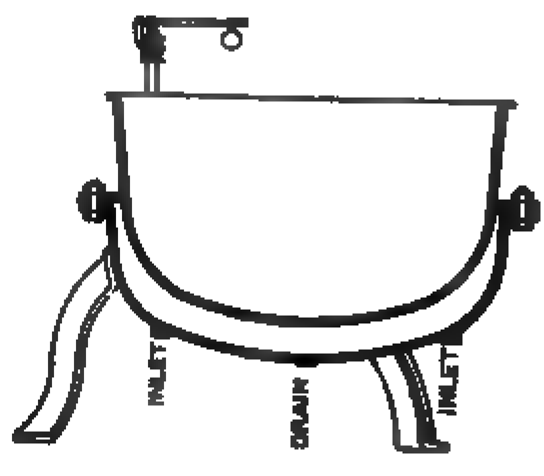

FIG. 24.—Steam-jacketed Kettle.

Evaporation under Reduced Pressure. There are many forms of apparatus employed for evaporation under reduced pressure, yet they all depend upon the same principle.

Vacuum Pan. The necessary equipment for this installation is a vacuum pan, condenser, receiver and pump. The pan is usually a globular copper or iron vessel, which is provided with a manhole, a discharge opening at the bottom, a thermometer, a vacuum gauge, peep holes, test cocks,

liquor gauge and catch all. In most of the larger pans the heating is accomplished by means of steam coils placed in the bottom of the pan, while the smaller sizes have a steam jacket. At the top of the pan is a dome or large pipe connected with the "catch-all" the purpose of which is to retain any liquid that may be carried along mechanically by the steam. A small pipe at the bottom of the catch-all returns the water to the still, while a larger one is connected to the condenser. The condenser is a tin-lined copper coil surrounded by running water. Joined to the condenser is the receiver, which, like the pan, is provided with a liquor gauge. Attached to the receiver is the pump which in this apparatus would be one working on the dry system. In many cases, however, it is not necessary to collect the liquid which passes off, so that it is possible to dispense with the condenser and employ a vacuum pump which works on the wet system. A wet-system pump is so constructed as to take care of all condensations without the aid of an extra condenser.

Multiple-effect System. The most efficient method of evaporation is that secured by means of the multiple-effect system. The apparatus usually consists of three or four vacuum pans, so arranged that the steam from the first pan passes through the coils or jacket of the next in line, and the steam generated in the second serves to heat the liquid in the third. The vacuum maintained in each of the pans increases as it approaches the pump for the reason that the condensations play quite an important part in producing reduced pressure. Thus it is that the pan having the highest temperature has the least vacuum, and that having the greatest vacuum has the least temperature. As a rule only three pans are employed, being known as triple effect, although sometimes four are used when they are known as quadruple effect.

Yaryan Evaporator. This apparatus consists of a large number of small tubes joined together in groups of six, each group of which is a unit. The tubes of each set are joined in such a manner as to form a continuous coil, each end of which is free, the whole being enclosed in an outside shell of boiler plate.

In the operation of this apparatus the steam is allowed to enter the cylindrical chamber surrounding the series of tubes. Either exhaust or pressure steam may be used, as desired. The solution to be concentrated is passed into the coils under pressure and being highly heated is converted into a mass of foam, which finally escapes from the last tube of the coil into the separator. Here it is discharged with considerable force against baffle plates, thus separating the liquid from the steam. The liquid collecting in the separator of the first effect is forced into the coil of the second effect, while the steam produced in the first effect is conducted into the chamber surrounding the tubes of the second effect, where its heat is utilized for further evaporation of the solution; and thus the operation is repeated throughout the entire system. The steam from the final effect is passed into a condenser, which in its turn is connected

to a vacuum pump, thus producing a high vacuum in the separating chamber and coils. Owing to this reduction in the boiling point of the liquid there is a condensation of the steam as it strikes the cooler pipes, thereby producing a less perfect vacuum in the preceding effect. Thus we have a gradual reduction of pressure and consequent lowering of the boiling-point from the time the liquid enters the first effect until it is discharged from the last. The condensed steam, *entrainments* from the chambers surrounding the coils, together with that from the condensers, is collected in many factories, and may be employed as feed-water for boilers or for other purposes. The ordinary form of vacuum pan will evaporate from eight to ten pounds of water per pound of coal, while it is claimed that the

Fig. 25.

triple-effect Yaryan will evaporate from twenty-three to twenty-five pounds, and the quadruple effect thirty pounds.

Lillie Evaporator.[1] The mode of operation which distinguishes the "Lillie" from other forms of apparatus is that the results obtained are due to film evaporation; that is to say, the liquid flows over the heated tubes rather than through them, thus exposing a very large surface for evaporation. In the older forms of multiple-effect apparatus some difficulty was encountered from liquids which deposit heavy incrustations on the heating surfaces. This difficulty, however, has been overcome in the new model. The new feature, which corrects this condition, is the reversal at will of the direction of the course of the vapors or heat through the multiple effect, making thereby, what before the reversal was the hottest effect the coolest, and what was the coolest the hottest. Fig. 25

[1] The Sugar Apparatus Manufacturing Co., Philadelphia, Pa.

shows a vertical longitudinal section through the body of the evaporator. The evaporating tubes slightly incline downward to the steam end and open through the heavy tube plate partition in which they are firmly expanded and by which they are supported. The other ends of the tubes are closed save for a small air vent in each. They are not fastened or supported in any way, and the tubes are quite free to expand or contract independently of the shell of the effect.

On the under side is a centrifugal circulating pump, located midway between the ends of the evaporator. The condensation from the steam in the tubes flows back into the steam end, and thence through a steam trap into the end of the next cooler body, and finally to the atmosphere from the coolest body, in the case of the multiple effect. The solution delivered by the centrifugal pump is forced on to a perforated distributing plate, from which it flows over the tubes in a deluging shower. The circulation in this case is independent of ebbulition, and there being no depth of solution on the tubes the vapors have a free passage for escape.

The method of heating and securing the reduced pressure is very similar to that of the Yaryan just described.

Distillation. This operation is usually for the purpose of separating liquids from other liquids, or from solids, and may be considered as a special form of evaporation. In fact, evaporation and distillation are often carried on simultaneously. Many forms of distilling apparatus are in use, although they all have three points in common: (1) The still or vessel holding the liquids to be heated, (2) the condensers or cooling apparatus, and (3) the receiver or vessel in which the distilled liquid collects Between the still and condenser is a spray catch, provided with baffle plates, which prevents any of the solution from being carried over mechanically by the vapor. By this means the liquid is returned to the still while the vapor passes along to the condenser. The apparatus shown is made of copper, the condenser worm being tin lined.

Column Still. The illustration, Fig. 26, represents one of the types of column stills in common use. The column or *dephlegmator* (*B*) is placed on top of the boiler (*A*) and is divided into chambers by means of plates, each of which has a dome or flat-covered opening, with an overflow pipe leading to the chamber below. The vapor from the boiling liquid passes up through the opening, where it bubbles out through the liquid on each plate. The heavier liquid which is condensed here flows down through the overflow pipes and into the boiler. Between the column and the condenser (*E*) is a series of U-tubes surrounded by a water-bath, which may be kept at any temperature desired. As the mixed vapors pass through these tubes, the high-boiling portions are condensed and returned to the column, while the lightest or more volatile liquid only passes through the coil in the condenser (*E*).

Coffey Still. This form of apparatus, Fig. 27, consists of two towers: (A) known as the *analyzer* and (B) the *rectifier*. Free steam is forced into A through the pipe (C), where it bubbles up through the liquid on the perforated plates (D, D) and out by the way of (E) into the rectifier (B). The liquid to be distilled is now pumped through the pipe (F) and

Fig. 26.—Column Still.

the coil (G, G), and is delivered into the analyzer by the pipe (H). The liquid in this way becomes heated by the steam surrounding the coil and is delivered hot to the analyzer. The hot liquid as it falls on the perforated plates spreads out in a thin layer, and runs down to the next compartment through the overflow pipe (J). The steam, as it passes up

Fig. 27.—Coffey Still.

through the layers of liquid, heats it very hot and carries the volatile portion over into the rectifier. During the passage of the mixed vapors up the rectifier the steam becomes condensed by contact with the cold pipes, thus allowing the more volatile portion to pass out through the pipe (K) to the condenser (L). The water which collects in the bottom

of the rectifier is pumped to the top of the analyzer through the pipe (*M*). From the bottom of the analyzer is a pipe (*N*) to act as a discharge for the spent liquor which has lost its volatile matter.

Conveying Solids. The man with a wheelbarrow is the simplest method of conveying solids, and is at the same time the least economical. A steel tray wheelbarrow weighs from 60 to 70 lbs., and will hold about 2 cu.ft. In a general way the laborer pushes the barrow through 200 ft. in a minute, and consumes about one and one-half minutes for loading and unloading. Larger barrows are made with two wheels, weighing from 200 to 250 lbs., and having a capacity of 8 to 9 cu.ft. As a rule barrows are used on level surfaces only, and are made of various shapes to adapt them for special purposes. In some cases it is advisable to lay steel tracks and draw the cars by means of electric motors or small locomotives. The arrangements for dumping the cars vary to some extent, but of the ones in common use may be mentioned the V-shaped dump car, the gabled or saddle-bottom dump car and the hinged-end dump car.

Cars which have to go up a steep incline may be hauled by a wire cable or run into an elevator. Endless chains or cables provided with catches to hold the car while it is being drawn up the incline are much used, especially for mining operations. An aerial cableway is often used where the country is rough and where it is necessary to cross a stream. The cable of wire or rope is suspended from towers. The cable is usually endless, and along it are run carriages to which skips or buckets are attached. Material may also be moved by the use of the revolving locomotive crane with clamshell bucket or other form of container. A very efficient form of transportation is by means of the belt conveyor. These belts are usually made of rubber or cotton. The rubber belts (cotton duck coated with rubber) are especially designed for rough usage, while the cotton belts are more often employed for the carrying of boxes and packages. The belts, which may be flat or troughed, are run on rollers for support; the motion being imparted by a head pulley, and the slack taken up by the foot pulley. Different types of rollers are used according as the belt is flat or trough shaped. The capacity of such a conveyor depends upon the width of the belt and its speed, a troughed belt being able to carry two or three times as much load as a flat one.

For the transportation of hot or very rough material bucket conveyors are generally employed. These buckets are carried on rollers and are joined together by a roller chain. Apron conveyors are made by attaching light strips of wood or metal to link chains, thus forming a continouus belt much used for handling light packages.

In drag or flight conveyors the material is pushed along, the simplest form being one in which the plain scraper is drawn by a central rope or wire. In the suspended draw conveyor the flights are attached to cross-bars having wearing shoes at either end which slide on angle-iron tracks. In the roller flight conveyor the shoes are replaced by rollers.

The screw conveyor consists of a shaft around which metal flights are bolted to form an endless screw, this shaft rotating in a trough pushes the material along.

When material is to be lifted any distance it is done by bucket elevators. The buckets are fastened to belting or link chains. A bucket shaped like the letter L is easily discharged, and is therefore largely used for conveying pasty material; those shaped like the letter V have a larger capacity, but do not empty so readily as the L-shaped. The buckets may be made of steel, malleable iron or copper, according to the use to which they are to be put. They are also sometimes perforated to allow the material to drain, while others have saw edges, as those used for lifting tanbark and such material. The belt to which the buckets are attached passes over two pulleys and the material is discharged by centrifugal force as it goes over the top one. For conveying barrels and boxes special elevators have been designed.

Conveying Liquids. The simplest problem which presents itself is the conveying of a liquid from a higher to a lower level, in this case gravity is the motive force; that is, the liquid is made to flow by means of a *head*. Liquids are usually conveyed in pipes which may be made of a variety of materials. For water galvanized, or cast iron, lead, copper, tin, and alloys as well as ebonite are used. Earthenware and cement pipe are used extensively for waste material. Glazed pipe or vitrified tile find application for acid liquids; they are rather fragile, however, and should not be exposed to over 20 lbs. pressure to the square inch. Wooden pipes which are made of staves bound together with steel bands are much used for beer, vinegar, organic acids and dilute mineral acids. Lead pipe is very valuable in chemical industry as it resists corrosion, but is not satisfactory when exposed to heat or pressure; for this reason iron pipes which are lead lined are much employed. Tin pipes are sometimes used in breweries, and for conveying distilled water, carbonated water, vinegar and wine; but owing to their expense tin-lined copper or iron pipes are more generally employed. Copper and brass pipes find extensive application, especially for conveying and use in the manufacture of dye-wood extracts and tanning materials. Wrought iron, either plain or galvanized, is used for the distribution of water, while cast-iron pipes are employed for conveying concentrated acids.

Elevating Liquids. The most common method of lifting liquids is by means of pumps, which may be driven by steam, electricity, water, belt or gear. The pressure secured in a plunger pump is due to the force of a piston, while in a centrifugal, Fig. 28, pump[1] the pressure is obtained through a rotary motion imparted by means of revolving fans. The pulsometer and hydraulic ram are used to a limited extent.

To withstand the action of acid and alkaline solutions, pumps are made of various materials; but for the elevation of more corrosive liquids

[1] Lobee Pump and Machinery Co., Buffalo, N. Y.

the acid egg is generally used. Acid eggs are usually made of acid-proof cast iron and heavy enough to withstand the necessary pressure; they are also sometimes made of earthenware. To operate, it is allowed to fill with the liquid, the ingress closed, then by the admission of compressed air the liquid is forced through a tube. The Harris system of elevating liquids by compressed air consists of two cylinders, opening into common

Fig. 28.

fill and discharge pipes, the cylinders being filled by suction and discharged by pressure.

Where a liquid is to be transferred from a higher to a lower level the siphon is the simplest and most economical appliance which can be used, The simplest method to start the flow is to fill both limbs with the solution.

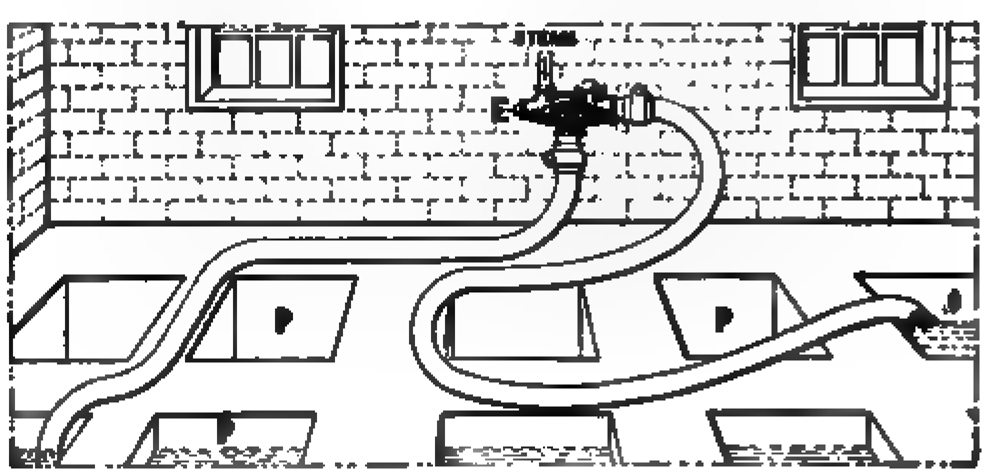

Fig. 29.

and plunge the short arm into the liquid contained in the upper vessel. A very convenient form of siphon can also be arranged by having a swivel pipe attached to the bottom of the tank, and lower it to the proper level by means of a chain.

Liquids are sometimes raised or conveyed by means of injectors which are usually operated by steam, and whose efficiency depends upon the principle of the difference in velocity of a jet of steam issuing from an orifice and that of a jet of water. The solutions raised by an injector become heated and diluted by the condensed steam.[1]

Conveying Gases. Gases, if valuable for manufacturing purposes as well as those which are of no use have to be conveyed from one part of the plant to another, or entirely removed, as the case may be. The pipes used for this purpose may be of sheet iron, galvanized iron, cast iron, or wrought iron, as well as flues of brick, concrete, and lead-lined wooden ones. Gas blowers and exhausters are made either to overcome a low counter-pressure or rarefaction such as blowers and ventilators; or to overcome high counter-pressure, or exhaust against a high rarefaction. These go under the name of compressors and exhausters. Fan blowers

Fig. 30.

consist of a number of blades fixed on a rapidly revolving shaft; they are only used where the counter-pressure is very slight. In pressure blowers the width of the blades are parallel with the shaft and enclosed in a casing, usually of metal. The higher the speed at which the blades revolve the greater the pressure.

Chimneys are often used to carry off noxious gases as well as to create a draft and promote combustion of fuel. For a good draft height is especially desirable, while for the removal of noxious gases size is perhaps the most important. Forced draft may be produced by blowing air through the flues or by exhausting the gases formed during combustion. That chimneys deliver noxious gases at a sufficient height to prevent deleterous action on vegetable and animal life should also be taken into consideration.

[1] Schulte & Koerting Co., Philadelphia, Pa.

Refrigeration. The principle involved in all refrigerating machines is the absorption of heat by the evaporation of a volatile liquid. The substances in most common use are liquefied ammonia, sulphur dioxide, and carbon dioxide. The one most commonly employed, however, is ammonia and it is used both in the *compression* and the *absorption* systems.

Compression System. The gas being heavily compressed is liquefied by passing it through coils over which cold water is allowed to flow; the liquid is then passed through a small opening into a large coil of pipe. The expansion of the ammonia from a liquid to a gaseous state causes the absorption of much heat, with the result that the temperature falls below the freezing-point of water. The gases formed in the expansion pipes are rapidly exhausted by means of a pump and returned to the compressor, where the cycle is repeated, it being necessary only to supply sufficient ammonia to replace that lost by leakage.

For the manufacture of artificial ice the expansion coils are surrounded with a strong brine or calcium-chloride solution, into which galvanized-iron boxes filled with water are immersed. When used for cold storage it is desirable to increase the cooling surface of the expansion coils. To do this cast iron disks are placed at frequent intervals on the pipe perpendicular to its line of direction, and the pipes suspended from the ceiling of the room.

Absorption System. The York Absorption Refrigerating Machine shown in the illustration, Fig. 31, consists of a generator, analyzer, dehydrator, ammonia condenser, ammonia receiver, exchanger, weak aqua cooler, absorber, strong aqua tank, aqua ammonia pump and pressure gauges. In operating this machine steam is admitted to the generator coils, thus heating the aqua ammonia to boiling. The liberated gas passes upward through the analyzer, which is mounted on top of the generator, where some of the water still left in suspension in the gas is removed by coming in direct contact with the incoming strong aqua ammonia from the absorber.

On leaving the analyzer the gas enters the top of the dehydrator, where the remaining water is condensed. The now anhydrous gas enters the ammonia condenser, where it is liquefied, and drawn into the anhydrous liquid ammonia receiver. From this receiver it is admitted to the evaporating coils in which the refrigerating effect is produced. The expanded gas from the evaporating coils then enters the absorber, where it comes in contact with weak aqua ammonia, thus producing a solution of strong aqua ammonia. The strong aqua ammonia overflows from the absorber into a strong aqua tank; the aqua ammnoia pump, taking its suction from this tank, discharges the strong aqua ammonia into the exchanger at the bottom of the shell. In passing through the exchanger the liquid becomes heated to within 35° to 40° F. of the temperature of the generator by the weak aqua ammonia from the generator. On leaving the exchanger the

FIG. 31.

strong aqua ammonia enters the top of the analyzer, where it is still further heated by passing over the baffle plates and coming in direct contact with the liberated gas from the generator. From the analyzer it enters the generator at very near the temperature due to the steam coils of the generator, is again boiled and the cycle repeated.

II

MATERIALS USED IN THE CONSTRUCTION AND OPERATION OF CHEMICAL PLANTS

A. B. AUBERT

Wood. Wood is especially valuable as a building material because of its strength, elasticity, and the ease with which it can be worked. The growing part of timber trees is confined to a thin layer, the cambium, which lies between the wood and the bark, and from which both are formed by cell division. The timber in a log is made up of a number of concentric rings which mark the annual growth. These rings surround the pith, the whole being protected by the bark. The medullary rays are radial lines which begin at the outer surface and pass toward the center. Wood cells vary somewhat in shape. They are usually elongated and packed close together, more or less incrusted and hardened with deposition of lignin. The living wood tissue contains from 50 to 70 per cent of water. This is greatest in amount in the young twigs and branches, and increases when the growth is most active. It is usual to fell trees in the winter or early spring, growth being then dormant and the quantity of sap less. The drier the wood the more durable it is as structural material. In the process of drying wood shrinks, the newer growths shrinking more than the older and, as the latter growths are outside, raidal cracks are formed. If planks are sawed out of wood before it has shrunk completely there will be warping upon subsequent drying, owing to the greater contraction of the newer wood.

Seasoning. Wood is seasoned by being so piled as to admit of free access of air; the process may last for several years, but it may be greatly shortened by exposing the wood to air heated to a temperature of 100° to 250° F.

Structural Application. Woods used for structural purposes may be classified into soft and hard. Soft woods are chiefly derived from the coniferous trees, while the leaf woods are more or less hard. Wood is very durable under proper conditions, but if exposed to adverse agencies, it decays rapidly.

Fungoid Growth. The most common of the diseases of wood is dry rot, which causes it to darken in color, to emit a musty odor, to become soft and finally to crumble to powder. This disease is due to a fungoid

growth, *Merulius lachrymans*, which in process of growing entirely destroys the wood fiber. The more thoroughly a wood is dried the less liable it is to the attacks of fungi. Dampness, darkness, and a certain degree of warmth are the conditions most favorable to the life of the fungus. To avoid dry rot well-seasoned lumber should be selected and it should, if possible, be placed so as to have access of air and freedom from moisture.

Wood Preservation. Protection of wood from fungi may be secured by the use of agents that destroy living organisms. Dry wood may be painted or covered with a protective coating. When wood is not thoroughly dry it is well to treat it with an antiseptic agent, such as creosote, mercuric chloride, copper sulphate, or zinc chloride. The wood has to be completely saturated with the solution, however. In Bethell's process the wood is air dried, heated for twenty-four hours at 160° F., and then transferred to an hermetically sealed iron cylinder from which the air is exhausted, and into which creosote oil is pumped at a temperature of about 150° F. with a pressure of about 170 lbs. per square inch. Soft wood absorbs 8 to 10 lbs. per cubic feet and hard wood less. In Rütger's process creosote and zinc chloride are used. In Kyan's process mercuric chloride is injected into the wood, while in Boucherie's process copper sulphate is used, and in Burnett's process zinc chloride.

Industrial Application. In the equipment of chemical plants the local timber best suited to the purpose may often be employed, although leaf woods are the most satisfactory and are generally used. Wood that is to be exposed to considerable heat is liable to shrink and warp, and on that account it should be well seasoned. Wood rich in resin, (pitch pine) should be selected for timber exposed to acid or other fumes, as the resin present acts as a protector. Cypress is the best wood for vats and tanks, as it is very durable, straight grained, does not warp much, and imparts no color or odor to liquids therein contained. White pine is used for water and brine tanks, while yellow pine is extensively employed in pulp mills for acid liquor. Yellow poplar, being close grained, is used for volatile liquids, it imparts neither taste nor odor to solutions and is, therefore, used in tanks for storage of alcoholic extracts. Tanks and vats made of wood cannot be used for alkaline solutions, as they attack and soften it, but neutral or very slightly alkaline solutions may be stored in them. Some neutral solutions have a corrosive action on wood, so that they will work their way through in time: iron, calcium, and magnesium salts especially have this property.

Wooden receptacles, if used for storage of liquids, should never be allowed to become dry, but should be filled with water when not in use; and in their construction no material should be used that will affect or be affected by the solutions which they are to hold.

Iron. In the construction of technical apparatus iron is of great value.

Cast Iron. Cast iron contains from 2½ to 4½ per cent of carbon, besides varying quantities of silicon and manganese. In gray cast iron most of the carbon is in the uncombined or graphitic form, while in white cast iron most of the carbon is combined and the percentage of manganese may be high.

Cast iron resists alkali solutions as well as alkali in a molten condition. It is only slightly acted upon by concentrated acid. Sulphuric acid above 1.7 sp.gr. can be concentrated in cast-iron stills. Weak acids, however, act readily upon cast iron. It may, nevertheless, be rendered passive by the action of strong nitric acid, so that it will then withstand the action of weak acids. Solutions of neutral salts that are not much dissociated do not attack cast iron readily, while others more dissociated attack it. Ammonium chloride, if evaporated in an iron vessel, rapidly attacks it.

Dry air does not affect iron to any extent, although moist air or intermittent contact with water easily rusts it. Wrought iron rusts more rapidly than cast iron. Iron may be protected by a coating of asphalt varnish, graphite paint, or red lead and oil.

Wrought Iron. Wrought iron is more rapidly attacked by acids, sulphides, and alkalies at high temperatures than is cast iron. When using cast and wrought iron together due allowance must be made for the greater coefficient of expansion of wrought iron. The tensile strength of wought iron and steel is greater than that of cast iron; while cast iron has greater crushing strength.

Enameled Iron-Granite or Agate Ware. Enameled iron is very useful for the construction of vessels as it combines the resistive properties of stoneware and the durability of metal. The enamel should have the same coefficient of expansion as iron so as to avoid the risk of cracking, thereby allowing the direct contact of the liquor with the metal underneath.

Lead. Next to iron lead is probably the most important metal to the technical chemist. It is not attacked to any extent by warm or cold sulphuric acid, provided the specific gravity is less than 1.7. Hydrochloric acid, and nitrie acid both dissolve lead, although it is not appreciably attacked by chlorine free from hydrochloric acid. It resists the action of dry, moist air. Water acts on it slowly as well as solutions of nitrates, nitrites, chlorides, tartrates, citrates, acetates, some ammonia compounds, and decaying organic matter. Sulphates and alkaline carbonates do not corrode it to any great extent. Lead in contact with other metals causes galvanic action, which may cause the destruction of the lead vessels. Lead vessels should not be embedded in cement, as the metal is likely to become brittle. Owing to the comparative weakness of lead it is usual to support it by an outside covering of wood or iron. Under the influence of heat lead expands in the usual manner, but does not contract in the same ratio on cooling; allowance, therefore, to avoid

bulging must be made for this peculiarity. Lead joints are made by the process of autogenous soldering (lead burning) which consists of fusing together the edges that are to be joined by the use of a hydrogen blowpipe. The hydrogen gas used should be pure and entirely free from arsenic or antimony compounds.

Copper. The uses of copper are more restricted than those of lead. It is readily affected by ammonia and acid fumes and ammonium sulphide. The common mineral acids dissolve it easily, while the weaker organic acids, such as lactic, tartaric and acetic have but little corrosive action. It is, therefore, more used in organic than in inorganic technology. It is a good conductor of heat and electricity, is malleable, and of considerable tensile strength; hence copper apparatus can be made with thinner walls than is possible with iron. It is employed in the manufacture of stills, condensers, and digestors. Joints in copper apparatus are riveted or brazed. This is done by the use of hard solder (3 parts copper and 1 part of zinc). The soldering is done by a blowpipe with borax as a flux.

Bronze. This is probably the most useful alloy of copper; it is only slightly attacked by dilute sulphuric acid. Phosphor bronze resists corrosion very well, as does also manganese bronze. Both of these may be used to a limited extent in the construction of chemical apparatus.

Tin. Tin is not readily oxidized at ordinary temperatures; water does not appreciably act on it, neither do dilute acids. Its principal use is for the worms of condensers and for lining copper vessels.

Aluminium. This metal is light in weight and easily worked. Air, water and hydrogen sulphide do not act on it. It is, however, attacked by caustic alkalies, mineral acids, solutions of chlorides and nitrates. Organic acids have but little action upon it, and it is used in the making of stills and worms for use in the manufacture of acetic acid. It forms valuable alloys with copper, such as aluminium bronze, which resists the action of many saline solutions. Alloyed with magnesium it forms magnalium, a white metal of low specific gravity, possessing great tensile strength, and which can be soldered.

Nickel. Nickel is a hard metal that can be welded. It is malleable and ductile and is not readily acted upon by atmospheric influences. Dilute acids attack it, while nitric acid renders it passive. Dilute alkaline solutions do not readily attack it, though strong lyes do.

Platinum. This metal is very malleable ductile and heavy (sp.gr. 21.5). For technical use it may be alloyed with about 2 per cent of iridium, which hardens and renders it somewhat less easily attacked. It stands high temperatures without melting. It is attacked by no single acid, although aqua regia dissolves it. Moist chlorine, fused alkalies, alkaline sulphides and caustic attack it readily. Combinations that liberate arsenic, phosphorus, or easily reducible oxides should not be heated in it. It readily alloys with tin, lead, zinc, bismuth, and

copper, forming alloys that are much more fusible than platinum. When platinum vessels have been used for some time and exhibit a grayish appearance they should be scoured with fine sand. Stains may be removed by melting potassium acid sulphate in the vessel. It is especially used for stills in the manufacture of sulphuric acid and hydrofluoric acid. The high cost, however, restricts the use of platinum for many technical purposes.

Silver. Silver is not very generally employed in technical work, but may be used for vessels in which alkalies are to be fused. The melting point of the metal being comparatively low, the heating should be gradually and carefully performed.

Antimony. An alloy of lead and antimony is harder than lead, and having acid-resisting properties is used for making valves and stopcocks used in sulphuric acid work.

Stone. Stone is of great value for building purposes owing to its power of resisting disintegrating agencies. The durability of stone exposed to extreme variations of temperature depends to a certain extent upon its porosity. Mechanical agencies, such as wind and the action of rain, are of secondary importance. Organic disintegrating agencies, such as growing organisms, may occasionally cause considerable damage. This is more particularly the case with limestone.

Stone offers very great resistance to compression. A weak sandstone will withstand a pressure of 100 tons to the square foot.

Working the Stone. Sedimentary stone which has been deposited in layers should be set with the bedding horizontal. Most stones harden or season when exposed to the air, probably in part due to loss of water.

Granite. The granites vary greatly in composition and properties. They are all crystalline, with crystals from an inch or more in length to microscopic size. Quartz, feldspar, and mica are the essential constituents of granite. Light-colored granite usually weathers more rapidly than the darker varieties. Granite is durable, but it is difficult to work. If pyrites (FeS_2) is present, rust often appears on exposure to weather and the granite is likely to undergo disintegration more rapidly. Dark fine-grained granites are the most resistant to weathering.

Sandstone. Sandstone consists of grains of sand held together by some cementing substance which exerts a great influence upon the resisting qualities of the stone. Siliceous sandstone are those in which the cementing substance is silica; ferruginous, in which the cement contains Fe_2O_3; calcareous sandstone, in which the cement is calcium carbonate ($CaCO_3$); feldspathic sandstone, in which the cement is feldspar. The siliceous sandstones resist weathering agencies, but are hard to work. When the cementing substance is calcareous it is easy to work, but does not stand weathering well. Stones that are to stand the action of acid liquors should be only slightly porous and contain no minerals, such as seams of calcium carbonate, that the acid could attack.

Slate. Slate is easily obtained in any thickness. Two-inch slabs are usually used for making vats; they are grooved and bolted together the joints being made tight by means of rubber packing, melted sulphur, or a cement of litharge and glycerine. Dilute acids act upon slate very slowly, but it is rapidly softened by concentrated acids. It is sometimes used in the construction of Deacon's chlorine chambers, and for electrolytic tanks.

Limestones. Limestones are composed of carbonates of calcium and magnesium, with small quantities of impurities, and being comparatively soft are not very durable. They vary in color and are used for building purposes.

Bricks. Red bricks are made from fairly clean clay, nearly free from lime and containing more or less iron oxide, to which their color is due. In setting bricks the binding material generally used is mortar, made by mixing slaked lime with sand, 1 cu.yd. of lime to 4 to 6 cu. yds. of sand, yielding 4 to 6 cu.yds. of mortar. If the brick is to be exposed to moisture as in water tanks, cement is used, and it is usually mixed with sand or mortar. Mortar shrinks on setting, while cement expands slightly. Bricks used for foundations of buildings or machinery are usually set in cement. When used as foundation for machinery, cement should be protected from oil, which has a disintegrating effect upon it.

Firebricks. Firebricks are designed to stand high temperatures, and are made from clay poor in iron, alkalies, lime, and magnesia. They contain from 50 to 70 per cent of silica, and as small a per cent of fluxing agent as possible (Fe_2O_3, CaO, MgO, Na_2O, K_2O, TiO_3). The grains should be coarse, as silica in fine grains does not stand high temperatures. The joints between firebricks are made with fireclay, which should approach in composition that of the brick. The clay is mixed with water to a thick paste, into which the bricks are dipped. A thin layer of fireclay adheres to the brick, which is then placed in position and forced close up against the adjoining brick. Firebricks can be obtained varying in composition, size and shape. They are generally used in combination with ordinary bricks, the firebrick being placed on the inside where the heat is great and the common brick forming the outside.

Special refractory brick are also on the market, made from magnesite bauxite, chrome iron ore, graphite, and carbon. Magnesite brick, being basic, are attacked by silica, but resist well in copper, lead, nickel, and silver furnaces. While bauxite and chrome-iron bricks, being very refractory, are used to line steel furnaces. Carbon brick, which consist of retort carbon, coke, graphite finely ground, mixed with tar and burnt, are used in electro-metallurgical furnaces; being good conductors of electricity and highly refractory. They are poor conductors of heat.

When a new furnace is started it should be gradually raised to the temperature to be maintained. When stopped it should be cooled gradually. This is done by letting the fire down slowly and closing all dampers to prevent the ingress of cold air.

Glass. Though fragile and liable to crack by changes of temperature, glass is much used for apparatus employed in the manufacture of acids and salts that attack metals. Glass pipes are used to conduct acid gases, such as hydrochloric acid, from the furnace to the condenser; also in the construction of Hart's nitric acid condenser. Glass vessels are sometimes used in the concentration of sulphuric acid. Soda-lime glass is mostly used at present, though Jena and similar glasses are being introduced and would be more used if the price were not so high. The glass is much less liable to crack by sudden changes of temperature, if it is composed, in part at least, of zinc boro-silicate. Alkalies dissolve glass, while acids and even water act very slowly upon it, but for manufacturing purposes glass may be considered as acid and water resisting. The heating, cooling, expansion, and contraction of glass also causes certain molecular changes in its structure. Glass vessels when set in a furnace should be so arranged as to allow for contraction and expansion by heat changes. To accomplish this the vessels may be placed in a sand bath.

Stone- and Earthenware. These vessels should be well salt glazed, as their resistance to the action of chemicals depends to a great extent upon the quality of the glaze. Well-glazed earthenware will stand hot acids, and it is generally made heavy enough to stand considerable rough usage. Earthenware apparatus should not be exposed to great and sudden changes of temperature.

India Rubber. Rubber is usally vulcanized and generally reinforced by canvas cloth, of which there may be several layers alternating with layers of rubber, thereby giving proper strength to the materials. Rubber is attacked by oxidizing agents and does not stand high temperatures, becoming either hard and brittle or soft and sticky. Concentrated acids will destroy rubber, while dilute acids act slowly upon it. Dilute cold alkaline solutions act upon it slowly, but hot concentrated solutions rapidly attack it.

Hard Rubber. This is used to some extent in the manufacture of acid pumps, pipes, valves, and acid cocks. It is light in weight, though not strong, and hydrofluoric acid is kept in hard rubber containers.

Asbestos. Commercial asbestos is obtained from a variety of amphibole, a silicate of calcium oxide and magnesium oxide, or from a variety of serpentine (crysotile), which is a hydrated silicate of magnesia. Though differing in chemical composition these minerals are very similar in physical properties. Amphibole asbestos is the more fusible, and crysotile asbestos is the stronger and more elastic. Asbestos is a non-conductor of heat and is used as a covering for steam pipes, furnaces, and boilers, as a fireproofing and to prevent loss of heat by radiation. Acids have

but little action on it, and it is used in making joints in apparatus for concentrated acids. It is found on the market in a variety of shapes, such as fiber, paper, board, cloth, and rope.

Cement. That most generally used in the United States is Portland cement, which is made by heating to incipient fusion an intimate mixture of calcium carbonate, and clay rich in silica and grinding the resulting product to extreme fineness. This fine powder, mixed with water soon passes from the plastic to the solid state, which process is termed "setting" and requires a few hours, while the process of hardening needs six months to a year for its completion. It is practically insoluble in water and hardens in its presence.

Concrete. This is usually made by mixing 1 part of cement with 3 parts of sand and 5 parts of gravel or broken stone. It is used in making foundations for machinery, floors, tanks, cisterns, and in the construction of buildings. By using cinder in the place of gravel, the concrete formed is lighter and softer, nails can be driven into it, but it is much weaker and should not be subjected to heavy strain. When concrete is used for the construction of vats or cisterns, it should be covered with a mixture of Portland cement 1 part of cement and 2 parts of sand; or 1 part of cement, 1 part of slaked lime, and 1 part of sand.

CEMENT FOR SPECIAL PURPOSES.[1]

Cement Waterproofing. Asphalt is the best coating for concrete or cement walls to make them waterproof. Oil-proof cement is a stiff paste of slightly diluted glycerine and litharge, mixed when needed, or a solution of sodium silicate 35° Bé. made into a stiff paste with precipitated calcium carbonate, magnesium carbonate, or white lead.

Acid-proof Cement.

No. I. Boiled linseed oil and fire clay.

No. II. Black putty made by mixing equa parts of gas tar, linseed oil, and dry china clay.

To Resist Hydrocarbon Gases.

Silicate of sodium 42° Bé. mixed with asbestos, clay or sand.

Chlorine Resistant.

Powdered glass, Portland cement and silicate of soda, of each one part, to which may be added a small amount of powdered slate.

Elastic Cement.

Equal parts of pure linseed oil and clean gum rubber are mixed, the rubber being first dissolved in the smallest possible amount of carbon disulphide.

[1] *Chem. Eng.*, Vol. III, p. 271.

General Cement.

Plaster of Paris mixed with asbestos, oatmeal, straw, plush trimmings, hair, broken stone, and other substances, used according to strain, temperature, and other conditions. A putty of flour and molasses is useful.

Marine Glue.

Gum rubber	1 part
Shellac	2 "
Pitch	3 "

All melted together at as low a temperature as possible.

Stone Cement.

Zinc or magnesium oxide	2 parts.
Zinc or magnesium chloride	1 "

Powdered stone as a dilutant.

Water to make a paste.

Iron Cement.

Iron filings	40 parts.
Manganese oxide	10 "
Ammonium chloride	1 "
Portland cement	20 to 40 parts

Water to form a paste.

Casein Cement.

A solution of casein in water glass.

Lute for Essence Stills.

Rye meal, plaster of Paris and water to form a paste.

The rye meal gives elasticity to the lute.

Dry clay and linseed oil gives an excellent lute, not very strong, but resisting the action of many chemicals. For gas fittings white lead ground in linseed oil, mixed with red lead, is good. Sulphur and powdered glass fused together, may be used for making or cementing cisterns, vats, etc., for chemical use.

Preservation of Structural Materials. Stone for structural purposes must be selected so as to stand the climate of the country in which it is to be used. Porous stone and brick may be made non-porous by the use of some fatty or oily varnish which will sink into it. These applications must be renewed from time to time. The varnishes generally used are drying oils, paraffins dissolved in naphtha, and soft soap, followed by a solution of an aluminium salt which forms insoluble salts of the fatty acids of the soap. The application of paint is the most common preservative used for brick. In a general way it may be stated

that the more finely divided the pigment the less porous will the coat of paint be. Sandstone may be successively treated with an alkaline silicate, which is allowed to dry, and then with a solution of a chloride of an alkaline earth. This forms the insoluble silicate of the alkaline earth. The solutions generally used are sodium silicate and calcium chloride. The sodium chloride formed is washed or weathered out.

In the selection of a paint for iron or steel, care should be taken that the compound selected does not excite electrical action, which would stimulate corrosion. The dichromates of the alkaline earths have a preservative action and pigments containing these have been found useful for protection of iron and steel. Venetian red is generally looked upon as a good pigment for iron. It is usually prepared by the calcination of a mixture of ferrous sulphate and lime. Thus prepared, the pigment contains calcium sulphate and perhaps free sulphuric acid in small quantities, together with small quantities of basic ferrous sulphate. Such a mixture would have a corroding action on iron even if no free sulphuric acid were present. The calcium sulphate in the presence of water would slowly dissolve and corrode the metal.

In general, all pigments which are liable to undergo dissociation may be considered unsafe for iron and steel.

Perfectly pure iron oxide is a satisfactory pigment. The natural oxide and earthy mixtures of the same are safer than those manufactured by the decomposition, by means of heat, of some salt of iron. Iron may also be protected by enameling. In the Bower-Barff process for the protection of iron the articles are heated in a muffle to about 1000° F. (538° C.) and superheated steam at about the same temperature is admitted to the muffle. The iron decomposes the steam and a coating of Fe_3O_4 is formed on the iron, which protects it as long as it lasts unbroken. In another process the iron articles are immersed in water and made the anode of an electric circuit, and a film of Fe_3O_4 is formed, which acts as protection to the metal. In Angus Smith's process for the protection of iron pipe, the pipe is cleaned very thoroughly, heated to 700° F. (371° C.) and dipped into a mixture of coal tar, pitch, and a little linseed oil and heated to 300° F. (149° C.). The pipes are dipped vertically, allowed to remain for a few minutes in the bath, then drained and cooled in a vertical position.

III

WATER FOR INDUSTRIAL PURPOSES

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Composition of Natural Waters. All natural waters contain, dissolved or suspended in them, more or less of all materials with which they have come into contact. Therefore absolutely pure water cannot be obtained for industrial purposes, and the fitness of a natural water for use in any given process depends on its content of other substances. The amounts of such substances is determined principally by the chemical composition and physical structure of the contact materials, temperature, pressure, and duration of contact, and the condition and amount of matter previously incorporated in the water.

In general water from regions of old rocks like granite are low in mineral content; those from regions of limestone are hard; those from regions of alkali deposits are high in sodium and potassium; and those from swampy regions are highly colored. Surface waters flowing through districts of easily disintegrated material like clay are muddy. The drainage from basins with low rainfall is more highly mineralized than that from more humid areas. Ground waters are usually higher in mineral content than surface waters in the same locality, though this superiority is somewhat counterbalanced by the fact that ground waters are usually clear, while surface waters are frequently very muddy. For these reasons the surface waters of New England and the extreme northwest are low in mineral content and fairly clear but often highly colored. The rivers of the southeastern States are somewhat more strongly mineralized and carry large quantities of fine suspended matter, while most of the streams in Mississippi River basin are muddy and very hard. The rivers in the semi-arid valleys west of the Rocky Mountains often contain much mineral matter, particularly alkali. The chemical composition of the water in some typical rivers of North America may be seen in the following table, in which the figures represent the average condition:

AVERAGE CHEMICAL COMPOSITION OF THE WATERS OF TYPICAL RIVERS.

(Parts per million.)

	St. Lawrence.	Androscoggin.	Hudson.	Alabama.	Mississippi.	Rio Grande.	Colorado.	Sacramento.
Suspended solids	Tr.	Tr.	16	100	600	2475	10580	102
Dissolved solids	134	48	108	82	166	791	707	113
Silica (SiO_2)	6.6	9.0	11	21	11	29	—	28
Iron (Fe)	.05	3.2*	.15	.53	.13	3.6*	—	.43
Calcium (Ca)	31	7.4	21	13	32	104	92	13
Magnesium (Mg)	7.2	1.1	3.8	2.9	8.4	23	23	6.7
Sodium and potassium (Na+K)	6.3	3.5	7.9	7.0	13	119	110	13
Carbonate radicle (CO_3)	2.9	—	.0	.0	.0	.0	.0	.0
Bicarbonate radicle (HCO_3)	116	—	73	48	111	178	230	74
Sulphate radicle (SO_4)	12	12	16	9.0	24	228	180	17
Nitrate radicle (NO_3)	.3	—	.8	.7	2.5	—	.7	.6
Chlorine (Cl)	7.7	2.3	4.0	2.3	9.7	164	130	5.4
Probable scale, including suspended matter	110	36	95	165	720	2853	10920	180
Probable scale, excluding suspended matter	110	36	79	65	120	378	340	78

* $Fe_2O_3 + Al_2O_3$.

An important feature that is often overlooked in projected industrial applications of water is the fluctuation in mineral content, for continual changes of conditions influencing solution result in varying mineralization of waters. Rivers are most strongly affected by this fluctuation, the variations amounting to 100 per cent from week to week in the mineral content even of waters in large rivers; streams are usually lower in dissolved solids and higher in suspended solids during floods, when the water is diluted by rain, and higher in dissolved solids and lower in suspended solids during droughts and frozen periods, when the greater part of the stream flow is derived from underground supplies. Shallow wells are influenced in like manner, though not to so great extent, and the quality of water from very deep wells often fluctuates appreciably. These marked changes are important because they necessitate continual adjustment of softening and clarifying reagents where waters are being purified, and they also make it impossible to determine definitely by single analyses the quality of natural waters, especially those from running streams.

Examination of Water. For purposes of examination the substances that may be present in water are classified as suspended matter, such as particles of clay, sand, or leaves, dissolved matter, either of mineral

[1] Figures taken from Water-supply Papers, U. S. Geo. Survey, Nos. 236, 237 and 274.

or organic origin, microscopic animals or plants, and bacteria. Microscopical examination gives information regarding small organisms likely to affect the quality, such as growths of *crenothrix*, *beggiatoa*, and other forms of similar nature. Bacteriological processes are employed to ascertain the probability of contracting disease from water and they find industrial application particularly in testing waters that are used in the manufacture of food materials. By physical tests color, odor, turbidity, or muddy appearance, taste, and temperature are determined.

Though all classes of tests are valuable in the examination of industrial waters, the chemical analysis is most important and the estimates commonly made in order to determine the amount and the nature of the mineral ingredients are as follows:

Common Determinations to Ascertain the Mineral Ingredients of Natural Waters.

Total suspended solids.	Free carbon dioxide.
Total dissolved solids.	Free hydrogen sulphide.
Total hardness.	Free acids.

(Dissolved Constituents.)

Silica (SiO_2)	Carbonate radicle (CO_3)
Iron (Fe)	Bicarbonate radicle (HCO_3)
Aluminium (Al)	Sulphate radicle (SO_4)
Calcium (Ca)	Nitrate radicle (NO_3)
Magnesium (Mg)	Chlorine (Cl)
Sodium (Na)	
Potass'um (K)	

These are measures of the substances most commonly present and most likely to affect the industrial value of water. The analytical methods by which these estimates are made have been so thoroughly described in text-books of chemistry that it is not necessary to repeat them here. The suspended matter usually is not analyzed, as it is sufficient for industrial purposes to know simply its amount, general character, and fineness. The latter condition is expressed numerically by the coefficient of fineness, the quotient obtained by dividing the weight of the suspended matter by the turbidity. Sodium and potassium frequently are not separated from each other, the total weight of them giving sufficient information.

To complete the catalogue, the chemical tests of sanitary analysis may be mentioned: namely, free and albuminoid ammonia, nitrites, dissolved oxygen, oxygen consumed, and organic nitrogen. The results of such tests are useful in measuring the amount of known pollution by organic matter or in measuring the extent of its removal by processes

of purification, but exclusive reliance should not be placed in them for demonstrating the presence or absence of polluting matter.

When the quality of any supply is to be determined, it is important that samples representing all normal conditions of the water be examined. Daily or weekly tests of surface waters over a long period must be made before the fluctuations of quality can be known, and samples of well water should be collected under different conditions of pumping and saturation of the water table. Such multiplication of tests is expensive, but it is more economical than hasty installation without adequate knowledge regarding the quality of the proposed supply.

Expression of Results. The results of microscopical and bacteriological tests are almost uniformly expressed as the number of organisms per cubic centimeter of water. Chemical analyses are reported in various units, the most common of which are grains per United States gallon, grains per Imperial gallon, parts per hundred thousand, and parts per million. Simplicity of computations, avoidance of cumbersome fractions, and certainty of the basic unit make the latter system especially satisfactory for practical purposes. It has been adopted by sanitary and research chemists and by many technical chemists, and the exclusive employment of this unit industrially is delayed only by more or less objectionable precedent. The following table of factors gives the relations between the different units:

FACTORS FOR RECOMPUTATION OF ANALYSES.

One grain per U. S. gallon multiplied by	17.1	equals parts	per million.
One grain per Imperial gallon multiplied by	14.3	"	"
One part per hundred thousand multiplied by	10.0	"	"
One pound per 1,000 gallons multiplied by	120.0	"	"
One English degree multiplied by	14.3	"	"

The analytical methods commonly employed in the examination of water permit the estimation of the elements and radicles that are present; they also permit the determination of the total amount of matter in solution and treatment with dilute alcohol effects more or less approximate separation of the incrusting from the non-incrusting constituents. Besides these data, however, ordinary chemical tests contribute little to knowledge regarding the chemical composition of waters, and consequently the exact amounts of the different salts in solution are largely matter for conjecture. Though such substances as sodium chloride, potassium carbonate, and magnesium sulphate are probably present, they are not determined as such, and with information only as to the amounts of the elements and radicles it becomes mathematically impossible correctly to apportion the bases among the acids. Therefore, rules for making combinations of the radicles are necessarily arbitrary, and reports of hypothetical combinations by different analysts are frequently so widely divergent as to be incapable of comparison with each other.

The ionic form of statement, or statement of the radicles determined, appeals particularly to those engaged in technical work because it presents the actual results for the consideration, criticism, and application of persons other than those making the tests. Analyses in this form can be compared directly with each other, and discussions based on them can be put in much more definite form than those based on purely hypothetical combinations.

Uses of Water. In judging the value of water from the data afforded by analysis it is necessary to consider the supply both in relation to the use to which it is to be put and in relation to other available supplies. Besides being used for drinking and for general domestic purposes, water is essential in steam making, paper making, starch manufacture, and many other industrial processes. For each of these applications the amounts of certain ingredients in the water determine its value and assist in its classification. For example, considerable iron in a water may be harmful in one process and harmless in another. The value of a water for another process may be directly measurable by the amount of suspended matter, the amount of dissolved matter not being significant. It is obvious that the chemical composition of other available supplies should be taken into consideration, because the best water that can be obtained at reasonable expense should be used. Therefore, the best practice is to consider the quality of the water in relation both to its application and to other local supplies.

Water for Boiler Use. The chief industrial use of water is for steam making and its value for that purpose depends primarily on the amount and the chemical character of the mineral matter dissolved and suspended in it. The troubles in boiler-room practice caused by the mineral constituents of natural waters are scale formation, corrosion, and priming.

Formation of Scale. Formation of scale is the deposition of mineral matter within the boiler shell, and the deposit is called incrustation, sediment, or sludge according to its texture and its position. When water is heated under pressure and concentrated by evaporation as in a steam boiler, certain substances go out of solution and solidify on the flues and crown sheets or within the tubes. These deposits cause increased fuel consumption because they are poor conductors of heat and increased cost of boiler repairs and attendance because they have to be removed. If the amount of scale is great or if it is allowed to accumulate, the boiler capacity is decreased and disastrous explosions are likely to occur. Formation of scale is the most common boiler trouble, probably one-fifth of the steam generators in this country being found defective on that account. Some idea of the importance of scale formation and of means of preventing it may be gained by considering the effect of a water like that of Mississippi River, which carries 120 parts per million of scale-forming ingredients after the suspended matter has been removed. If such water were used without condensers under ordinary conditions

in a plant developing 1,000 horse power, besides the increased cost of fuel, maintenance, and depreciation, the scale itself would amount to a ton in twenty working days of twenty-four hours each, and this mass would have to be shoveled, scraped, and hammered from the inside of the boiler.

The scale or incrustation consists of the substances that are insoluble in the feed-water or become so within the boiler under conditions of ordinary operation. It includes practically all the suspended matter; the silica, probably precipitated as the oxide; the iron and aluminium, appearing in the scale as oxides or hydrated oxides; the calcium, precipitated in the form of carbonate and sulphate; and the magnesium found in the deposits principally as the oxide but partly as the carbonate. The scale constituted by these substances is, therefore, a mixture of compounds, which varies in amount, density, hardness, and composition with different conditions of water supply, steam pressure, type of boiler, and other circumstances. Calcium and magnesium are the principal basic substances in the scale, over 90 per cent of which usually is calcium, magnesium, carbonates, and sulphates. If much organic matter is present part of it is precipitated with the mineral scale, as the organic matter is decomposed by heat or by reaction with other substances. If magnesium and sulphates are comparatively low or if suspended matter is comparatively high the scale is soft and bulky and may be in the form of sludge that can be blown or washed from the boiler. On the other hand a clear water relatively high in magnesium and sulphates may produce a hard, compact scale that is nearly as dense as porcelain, clings to the tubes, and offers great resistance to the transmission of heat. Therefore the value of a water for boiler use depends not only on the quantity of scale produced by it but also on the physical structure of the scale.

Corrosion. Corrosion, or "pitting," is caused chiefly by the solvent action of acids on the iron of the boiler. Free acids capable of dissolving iron occur in some natural waters, especially in the drainage from coal mines, which usually contains free sulphuric acid. Some factory wastes carry free acids into streams. Many ground waters contain free hydrogen sulphide, a gas that readily attacks boilers; and dissolved oxygen and free carbon dioxide also are corrosive in their action. Organic matter is probably a source of acids, for it is well known that waters high in organic matter and low in calcium and magnesium are corrosive, though the exact nature and action of the organic bodies are not understood. Acids freed in the boiler by the deposition of basic radicles as hydrates are the most important cause of corrosive action. Iron, aluminium, and magnesium are precipitated as hydrates that are later partly or completely converted into oxides. According to the chemical composition of the water the acid radicles that were in equilibrium with these bases may do one or all of three things: they may pass into equilibrium

with other bases, displacing equivalent proportions of carbonates and bicarbonates, or they may decompose carbonates that have been precipitated as scale, or they may combine with the iron of the boiler, thus causing corrosion. If these acids exceed the amount required to decompose the carbonate and bicarbonate radicles present the iron of the boiler is attacked, and the results are pits or tuberculations of the interior surface, leaks, particularly around rivets, and consequent deterioration of the boiler.

Priming. Priming is the passage of water mixed with steam from the boiler, and it is intimately connected with foaming, which is the formation of masses of bubbles on the surface of the water in the boiler and in the steam space above the water. Foaming results when anything prevents the free escape of steam from the water. It may be due to particles of suspended matter, but usually the principal cause is an excess of dissolved substances that increases the surface tension of the liquid, thereby reducing the readiness with which the steam bubbles can break. Therefore, the tendency of a water to foam varies inversely with the concentration it will undergo before developing an excessive surface tension. As the sodium and potassium salts remain dissolved in the boiler water while the greater portion of the other substances is precipitated, the foaming tendency is commonly measured by the degree of concentration of the alkaline salts in solution, because this figure in connection with the type of boiler determines the length of time a boiler may run without danger of foaming.

Remedies for Boiler Troubles. The best remedy for troubles caused by substances in feed-waters is treatment of supplies before they enter boilers; this subject is considered under "Water Purification" (page 59). When such treatment cannot be given there are various ways of reducing potential injury. Low-pressure, large-flue boilers are frequently used in stationary plants supplied with hard waters, and it is said that the scale formed in them is softer and more flocculent and can therefore be more readily removed than that in high-pressure boilers. Blowing off is about the only practical means of preventing foaming, because this trouble is due principally to concentration of soluble salts in the residual water of the boilers. Accumulated sludge, or soft scale, can be removed by blowing, particularly in locomotive practice. In condensing systems much of the trouble due to mineral matter in the feed-water is obviated because the quantity of raw water supplied is proportionately small. The problem is not completely solved in such systems, because the incrusting or corrosive action is transferred from the boiler to the condenser, which requires more or less cleaning and repairing in proportion to the undesirable qualities of the water supply.

Boiler Compounds. Boiler compounds are widely used in regions where hard waters abound, but treatment within the boiler should be given only when it is impossible to purify the supply before it enters the boiler.

If previous purification is not practicable the feed-water frequently can be improved by judicious addition of chemicals. Many substances, ranging from flour, oatmeal, and sliced potatoes to barium and chromium salts, have been recommended for such use, but only a few have proved to be really economical. These substances have been classified according to their action within the boiler.[1] Those that attack chemically the scaling and corroding constituents precipitate the incrusting matter and neutralize acids. Soda ash, the commercial form of sodium carbonate, containing about 95 per cent Na_2CO_3, is the most valuable substance of this character, because it is cheap and because its use is attended with the least objectionable results. Tannin and tannin compounds are also used for the same purpose. The addition of limewater to the feed-water to prevent corrosion and to obviate foaming has been recommended,[2] and it is probable that lime used with waters high in organic matter and very low in incrustants would improve them. Such practice increases the incrustants in proportion to the lime added but prevents destruction of the boiler by corrosion. When soda ash is used it neutralizes free acids and obviates the precipitation of calcium sulphate by causing the precipitation of calcium carbonate. At the same time the sodium content of the feed is increased in proportion to the amount of soda ash. Its use results in the neutralization of acids, in the precipitation of the incrusting ingredients in a softer, more flocculent form, thus facilitating their removal, and in the increase of the foaming tendency of the water by increasing its content of dissolved matter. The second class of boiler compounds comprises those that act mechanically on the precipitated crystals of scale-making matter soon after they are formed, surrounding them and robbing them of their cement-like action. Glutinous, starchy, and oily substances belong to this class, but they are not now used to any considerable extent, because they thicken and foul the water more than they prevent the formation of hard scale. The third class comprises those that act mechanically, like those of the second class, and also partly dissolve deposited scale, thus loosening it and aiding in its ready removal. Kerosene is the most effective of such materials.

Many boiler compounds possessing or supposed to possess one or more of the functions just described are on the market and the sale of them is very great. Some are effective and some are positively injurious. Most of them depend for their chief action on soda ash, petroleum, or a vegetable extract, but all are costly compared with lime and soda ash. It can be readily understood that boiler compounds cannot in any manner reduce the total amount of scale but may increase it. Their only legitimate functions are to prevent deposition of hard scale

[1] Cary, A. A., The Use of Boiler Compounds, *Am. Machinist*, Vol. XXII, Part II, 1899, p. 1153.

[2] Palmer, Chase, Quality of the Underground Waters in the Blue-grass Region of Kentucky. Water-Supply Paper, U. S. Geol. Survey, No. 233, 1909, p. 187.

and to remove accumulations of scale that have attached themselves to the iron of the boiler. It should always be borne in mind that a steam boiler is an expensive piece of apparatus and that fuel and boiler repairs also are expensive. It is far more economical to have the water supply analyzed and to treat it effectively by certain well-known chemicals in proper proportion, either within or without the boiler, than to experiment with compounds of unknown composition.

Numerical Standards. The value of natural waters for boiler use depends primarily on their corroding and foaming tendencies and on the amount and character of scale likely to be deposited by them, but this value should always be considered in connection with local standards, for no matter how low a water may be in undesirable constituents it cannot be classed as good if it is poorer in quality than the average water of the region in which it occurs. On the other hand, if the best available supply is of poor quality the economy of purifying it even at large expense is obvious. In Maine, for example, where waters containing less than 100 parts of scale-forming ingredients are extremely common, a supply carrying 200 parts of such substances would not be classed even as fair for boiler use, but in Indiana such a supply would be classed as good, because in the latter State it is very difficult to find any natural water not exceeding 100 parts in scale-forming constituents. This illustrates the uncertain significance of local descriptive epithets, but it also emphasizes the fact that relative, not literal, translations of numerical standards should always be made.

Stabler,[1] in his excellent mathematical discussion of the quality of waters with reference to industrial uses, gives several formulas by which waters may be classified. His method of calculating the amount and the character of the scale likely to result from use of a water are quoted with the formulas recomputed to give results in parts per million.

$$A = \mathrm{Sm} + \mathrm{Cm} + 1.3\mathrm{Fe} + 1.9\mathrm{Al} + 1.66\mathrm{Mg} + 2.95\mathrm{Ca},$$

$$B = \mathrm{SiO_2} + 1.66\mathrm{Mg} + 1.92\mathrm{Cl} + 1.42\mathrm{SO_4} - 2.95\mathrm{Na} - 1.74\mathrm{K},$$

$$b = \frac{B}{A}.$$

A represents parts per million of total scale and B parts per million of hard scale. Sm, Cm, Fe, Al, Mg, and Ca represent respectively the amounts in parts per million of suspended matter, colloidal matter (silica plus oxides of iron and aluminium), iron, aluminium, magnesium, and calcium in the water. In the first formula calcium should not exceed $.668\ CO_3 + .328\ HCO_3 + .417\ SO_4$, in which CO_3, HCO_3, and SO_4 represent respectively the amounts in parts per million of the carbonate,

[1] Stabler, Herman, The Mineral Analysis of Water for Industrial Purposes and its Interpretation by the Engineer. *Eng. News*, Vol. LX, 1908, p. 355.

bicarbonate, and sulphate radicles. It is sometimes uncertain whether iron and aluminium are in solution or in colloidal state, but in applying this formula little error is introduced in assuming that Cm equals silica only. If no values are given for silica, iron, or aluminium, Cm may be taken as 20 and Fe and Al as zero without introducing great error. In the second formula SiO_2, Mg, Cl, SO_4, Na, and K represent respectively parts per million of silica, magnesium, chlorides, sulphates, sodium, and potassium. If the alkalies are not separated, the figure representing sodium and potassium together and computed as sodium may be used with the sodium coefficient in place of the last two terms of this formula. The ratio (b) between the amount of hard scale and total amount of scale is an index of the probable hardness of the scale. If b is not more than 0.25 the scale may be classed as soft; if between 0.25 and 0.5 as medium; and if more than 0.5 as hard.

Two and one-half times the total amount of sodium and potassium in the water is a sufficiently accurate estimate of the foaming constituents. For other formulas and comments on those quoted here Stabler's original article should be consulted.

The committee on water service of the American Railway Engineering and Maintenance of Way Association have offered a classification of waters in their raw state that may be employed for approximate purposes, but, as their report states, "it is difficult to define by analysis sharply the line between good and bad water for steam-making purposes."

APPROXIMATE CLASSIFICATION OF WATERS FOR BOILER USE

Incrusting and corroding constituents.* Parts per million.		Classification.
More than	Not more than	
—	90	Good
90	200	Fair
200	430	Poor
430	680	Bad
680	—	Very bad

* Proc. Am. Ry. Eng. and Maintenance of Way Assoc., Vol. V, 1904, page 595.

Foaming constituents.* Parts per million.		Classification.
More than	Not more than	
—	70	Very good
70	150	Good
150	250	Fair
250	400	Bad
400	—	Very bad

* Idem, Vol. IX, 1908, p. 134.

The limit of 90 parts of incrusting and corroding constituents for the class of good waters restricts perfectly acceptable natural waters to a small number, but the choice of that figure was probably influenced by the fact that the incrustants in poorer waters can usually be reduced by proper treatment to that amount. The limits must be interpreted liberally in practice, because they are modified by the comparative hardness of the incrustation and the different extent of corrosion effected by waters of the same mineral content but of different chemical composition. Waters of the worst class may be improved by treatment in softening plants.

The question how hard a water may be used without treatment can be decided by comparing the cost of artificially softening the water with the saving effected by the use of softened water.

The benefits include:

Saving in boiler cleaning.
Saving in boiler repairs.
Saving in fuel due to decrease in scale.
Increased number of boilers in service.
Decreased depreciation of boilers.
Value of materials removed by softening plant.

The cost of softening includes:

Labor for operating softener.
Power for operating softener.
Softening chemicals.
Interest on cost of installation.
Depreciation of softening plant.
Waste in changing boiler water due to increased foaming tendency of the water.

In general it is economical to treat waters containing 250 to 850 parts per million of incrustants, and those containing less than the lower amount if the scale contains much sulphates. As the incrusting solids may commonly be reduced to 80 or 90 parts per million the economy of treating boiler waters deserves careful consideration in region of hard water.

The amount of mineral matter that makes a water unfit for boiler use depends on the combined effect in boilers of the softening reagent used with such waters and of the constituents not removed by softening, Sodium salts added to remove incrustants or to prevent corrosion increase the foaming tendency, and this increase may be great enough to render a water useless for steaming purposes. It is not of much benefit to soften a water containing more than 850 parts per million

of non-incrusting material and much incrusting sulphates. Trouble from foaming in locomotive boilers begins at a concentration of about 1,700 parts per million of foaming constituents and a concentration of 7,000 parts is about the limit of safety for stationary boilers. Though waters containing as high as 1,700 parts per million of foaming constituents have been used, it is usually more economical to incur considerable expense in replacing such supplies by better ones.

Water for Industrial Use other than Boiler Purposes. The manufacture of many articles is affected by the ingredients of natural waters. The quality of water for boiler service has already been discussed; with reference to factories it need only be added that increase of boiler efficiency often justifies purification of poor water when increased value of the manufactured product alone may not be considered to do so. This observation applies particularly to paper, pulp, and strawboard mills, laundries, and other establishments where large quantities of water are evaporated to furnish steam for drying, and to ice factories and similar plants where distilled water is produced. But besides its use for steam making water plays a specific part in many manufacturing processes. In paper mills, strawboard mills, bleacheries, dyeworks, canning factories, pickle factories, creameries, slaughter houses, packing houses, nitroglycerin factories, distilleries, breweries, woolen mills, starch works, sugar works, tanneries, glue factories, soap factories, and chemical works water becomes a part of the product or is essential in its manufacture. As the principal function of water in most of these establishments is that of a cleansing agent or a vehicle for other substances, a supply free from color, odor, suspended matter, microscopic organisms, and especially bacteria of fecal origin, and fairly low in dissolved substances, especially iron, generally is satisfactory; but there are some exceptions. Water hygienically acceptable is necessary where it comes into contact with or forms part of food materials, as in the making of beverages and dairy or meat products. As all these ideal conditions are infrequently encountered in natural supplies, the manufacturer is confronted with the problems of ascertaining what degree of freedom from these substances is necessary to prevent injury to his machinery or to his output and whether the cost of obtaining such purity is counterbalanced by decreased cost of production and increased value of product. Competitive business methods and increased facilities of transportation have standardized the values of manufactured articles so thoroughly that makers are now obliged to scrutinize carefully every item of production costs in order to obtain reasonable profits. Therefore any appreciable saving effected by improvement of the water supply is one of the easiest sources of profit for the manufacturer.

The effect in some industries of the substances most commonly found in water are here outlined. The treatment is not exhaustive, the object being to offer approximate standards to aid in classification.

Effect of Free Acids. Free mineral acids, such as sulphuric acid in drainage from coal mines or hydrochloric acid in the effluents of some industrial establishments, are especially injurious and nearly always necessitate purification. In paper mills, cotton mills, bleacheries, and dyeworks, acids decompose chemicals and streak the fabrics besides rotting them. They also corrode metal work, rapidly destroying screens, strainers, and pipes. Such effects are likely to follow the use of water that contains a measurable amount of free mineral acid.

Effect of Suspended Matter. Suspended matter in surface waters may be of vegetable, mineral, or animal origin, consisting of particles of sewage, bits of leaves, sawdust, and sticks, or sand and clay. The silt so common in rivers of the West is largely derived from sand and clay. Few well waters contain suspended animal or vegetable matter, but many carry finely divided sand and clay, and they frequently become turbid by precipitation of dissolved ingredients. Suspended matter is objectionable in all processes in which water is used for washing and where it comes into contact with food materials, because it is likely to stain or spot the product. On that account suspended matter due to precipitated iron is especially injurious even in small amount. Small amounts (10 to 20 parts per million) of suspended vegetable or animal matter liable to decomposition or to partial solution are much more objectionable than equal quantities of mineral matter. For these reasons water should be freed from suspended matter before being used for laundering, bleaching, wool scouring, paper making, dyeing, starch and sugar making, brewing, distilling, and similar processes. In making the coarser grades of paper, such as strawboard, a small amount of suspended matter is not especially injurious, but for the finer white or colored varieties clear water is essential.

Effect of Color. Color in water is due principally to solution of vegetable matter, and materials bleached, washed, or dyed with light shades in colored water are likely to become tinged. Highly colored waters can be used in making wrapping or dark-tinted papers but not the white grades, and paper manufacturers are put to great expense for water purification on that account. The lower waters are in color, therefore, the more desirable they are for use in bleacheries, dyeworks, paper mills, and other factories where fabrics are likely to acquire undesirable brown tints.

Effect of Iron. Iron is the most undesirable dissolved constituent and comparatively small quantites of it necessitate purification. Many ground waters contain 1 to 20 parts per million of iron, which may be precipitated by exposure to the air and by release of hydrostatic pressure, causing the waters to become turbid, and such waters often develop growths of *crenothrix* that interfere in many industrial operations. In all cleansing processes, especially if soap or alkali is used, precipitated iron is likely to cause rusty or dull spots. In contact with materials containing tannin

compounds iron forms greenish or black substances that discolor the product. Therefore waters containing amounts even as small as 1 or 2 parts per million of iron frequently have to be purified before they can be used industrially. In water for dyeworks iron is especially objectionable and it commonly prevents the use of the water without purification.[1] Iron in the water supply of paper mills may be precipitated on the pulp, giving it a brown color, or during sizing or tinting, giving spotty effects. Water containing much iron cannot be used in bleaching fabrics, because salts that spot the goods are formed. The dark-colored compounds that iron forms with tannin discolor hides in tanning and barley in malting, and also give beer bad color, odor, and taste.[2]

Effect of Calcium and Magnesium. Calcium and magnesium are similar in their industrial effects and the amounts of them bear relation to each other, most natural waters carrying 10 to 50 per cent as much magnesium as calcium. In boiling processes some calcium and magnesium are precipitated on whatever is boiled in the water and this deposit may interfere with later operations. As these two basic substances decompose equivalent amounts of many chemicals employed in technical operations they are a cause of waste, and the alkaline-earth compounds thus formed on fabrics also interfere with later treatment. Some of the chemicals used to disintegrate the fibers in making pulp are consumed by the calcium and magnesium in the water supply, but the loss from this source is not nearly so great as that occurring later when the resin soap used in sizing the paper is decomposed by the calcium and magnesium. The insoluble soaps thus created do not fix themselves on the fibers but form clots and streaks. Similar decomposition of valuable cleansing materials and subsequent deposition of insoluble compounds take place in laundering, wool scouring, and like processes. In the manufacture of soap, calcium and magnesium form, with the fatty acids, curdy precipitates that are insoluble in water and therefore have no cleansing value. Many dyeing operations are interfered with by calcium and magnesium, which neutralize chemicals and change the reaction of the baths besides forming insoluble compounds with many dyes. Highly calcareous waters cannot be used for boiling the grain in distilleries because proper action is hindered by deposition of alkaline-earth salts on the particles of grain, nor for diluting spirits because they cause turbidity.[3] Very soft water, on the other hand, is said to be undesirable in paper mills for loading papers with any form of calcium sulphate because such waters dissolve part of the loading materials.[4]

[1] Sadtler, S. P., A Hand-book of Industrial Organic Chemistry. Philadelphia, 1900, p. 483.

[2] De la Coux, M. A., L'eau dans l'industrie. Paris, 1900, pp. 187 and 232.

[3] De la Coux, op. cit., p. 251.

[4] Cross, C. F., and Bevan, E. J., A Text-book on Paper-making. New York, 1900, p. 294.

Probably waters high in chlorides would also be bad for this purpose as chlorides increase the solubility of calcium sulphate.

Effect of Carbonates. The effects of carbonates and bicarbonates on industrial waters are commonly not differentiated. It is not unusual to estimate the combined carbonic acid and to state it as the carbonate without distinguishing between carbonates (CO_3) and bicarbonates (HCO_3), though in many natural waters the carbonate radicle is absent and the combined carbonic acid is wholly in the form of bicarbonates. If hard waters proportionately high in carbonates and low in sulphates are boiled, the bicarbonate radicle is decomposed, free carbonic acid is given off, and the greater part of the calcium and magnesium is precipitated. For this reason waters of that character are generally more desirable for industrial operations than waters high in sulphates and low in carbonates, as boiling does not greatly reduce the amount of the hardening constituents under the latter conditions. In the manufacture of beer, waters high in carbonates are said to produce dark-colored beers with a pronounced malt flavor because the carbonates increase the solubility of the nitrogenous bodies, whereas waters high in sulphates yield pale beers with a definite hop flavor because the sulphates reduce the solubility of the malt and the coloring matters.[1]

Effect of Sulphates. The influence of sulphates in beer-making has been noted. Hard waters with sulphates predominating are desirable in tanning heavy hides because they swell the skins, exposing more surface for the action of the tan liquors.[2] Sulphates interfere with crystallization in sugar-making by increasing the amount of sugar retained in the mother liquor.

Effect of Chlorides. High chlorides are usually accompanied by high alkalies. Appreciable amounts of chlorides are injurious in many industrial processes, and this is particularly unfortunate, as no practicable way of removing or reducing this radicle has been discovered except distillation. Beverages and food products, of course, cannot be treated with water very high in chlorides without becoming salty. In tanning operations chlorides cause the hides to become thin and flabby.[3] Animal charcoal used in clarifying sugar is robbed of its bleaching power by absorption of salt, and chloride-bearing waters also affect the quality of sugars because saline salts are incorporated in the crystals.[4] In the preparation of alcoholic beverages chlorides in large amount prevent the growth of the yeast and interfere with the germination of the grain.

Effect of Organic Matter. Organic matter of fecal origin is of course dangerous in any water supply that comes into contact with food

[1] Brewing Water, its Defects and Remedies. American Burtonizing Co., New York, 1909, p. 19.

[2] Parker, H. N., Stream Pollution in Potomac River Basin. Water-Supply Paper U. S. Geol. Survey, No. 192, 1907, p. 194.

[3] Parker, H. N., idem.

[4] De la Coux, op. cit., p. 152.

products, and water so polluted should be purified before being used. Care in this respect is particularly necessary in creameries, slaughter houses, canneries, pickle factories, distilleries, breweries, and sugar factories. Organic matter not necessarily capable of producing disease is undesirable in other industrial supplies because it induces decomposition in organic materials like cloth, yarn, starch, meat, or paper, rotting and discoloring them, and because it causes slime spots on fabrics by supporting algæ growths.

Effect of Hydrogen Sulphide. Hydrogen sulphide occurs in some underground waters. It is corrosive even in small quantities, and it also injures materials by discoloring and rotting them. This substance is associated with so much dissolved salts in many waters that they are unfitted for industrial use for reasons other than their gaseous content.

Effect of Other Substances. Silica and aluminium are usually not present in sufficient quantity to have any appreciable effect in industrial processes except when water is evaporated. Large quantities of sodium and potassium, by adding to the amount of dissolved matter, are objectionable in some manufacturing operations. Phosphates, nitrates, and some substances not noted in this outline interfere with industrial chemical reactions, but they are seldom present in natural waters in sufficient quantity to have noticeable effect.

Potable Water. Water that is used on food materials in any industrial operation should be potable; that is, should be palatable, esthetically unobjectionable, and absolutely free from anything that might cause disease. Increased public attention to the quality of foods and beverages makes this standard essential and it is an extremely short-sighted manufacturer that disregards it. Because of this and because employees in many establishments use the mill supply for drinking, it is not out of place to note the requisites of water as a beverage.

To be entirely acceptable in this respect water should be free from suspended matter, color, odor, and taste, and fairly cool. It should be free from disease-bearing germs and poisonous chemicals; and it should be low in dissolved mineral ingredients. The nearer a water approaches these conditions the more satisfactory it is for general use.

Physical Qualities. Suspended mineral matter clogs pipes, valves, and faucets, and growths of microscopic plants suspended in water frequently cause bad odors and stains in clothes. Color is usually due to dissolved vegetable matter and is a cause of serious objection in a domestic supply only when it exceeds 20 or 30 parts per million. Some waters, especially those containing iron, develop a turbidity of 10 to 30 parts per million on exposure to the air, due to precipitation of dissolved matter, and such condition gives rise to an apparent though not a real color. Odors may be caused by various conditions. One like that of rotten eggs is due to free hydrogen sulphide. Growths of microscopic organisms in tanks and water mains often have unpleasant odors that make the water

objectionable. Perfectly acceptable drinking supplies are free from color, odor, taste, and turbidity.

Bacteriological Qualities. Before a water is used for domestic purposes there should be reasonable certainty that it is free from disease-bearing organisms. Yet present bacteriological technique does not permit positive statement regarding the presence or absence of such organisms, and it is advisable, therefore, to guard supplies against all chances of infection. The disease germs most commonly carried by water are those of typhoid fever. The bacilli enter the supply from some spot infected by the discharges of a person sick with this disease and though the germs are comparatively short-lived in water, they persist in fecal deposits for remarkable lengths of time and retain their power to infect water. Consequently wells should be so located that their waters are guarded against the entrance of filth of any kind either over the top or by infiltration, and pumps and piping in the system should also be protected. Water from a carefully cased well over 20 or 30 feet deep is acceptable if the well is located after the exercise of reasonable judgment in regard to privies, cesspools, and other sources of pollution. Open dug wells and the pits often constructed as reservoirs around the tops of casings are frequently exposed to fecal contamination from above or through cracks in poorly-built sidewalls. Care should be taken that the casings of deep wells do not become leaky near the surface of the ground so as to allow pollution to enter. As a matter of ordinary precaution the ground should be kept clean and water should not be allowed to become foul or stagnant near any well, no matter how deep it is. If shallow dug wells are necessary they should be constructed with water-tight casings extending down into the well as far as practicable and also a short distance above ground. The floor, or curbing, should be water-tight, and pumps should be used in preference to buckets for raising the water. Every possible precaution should be taken to prevent feet scrapings and similar dirt from getting into the water by way of the top of the well. Underground water is not only less likely to become contaminated if protected from surface washings, air, and light, but it keeps better and is less likely to develop microscopic plants that give it a bad taste.

Chemical Qualities. Amounts of dissolved substances permissible in a domestic supply depend much on their nature. No more than traces of barium, copper, zinc, or lead should be present because these substances are poisonous. The occurrence of these elements in measurable amounts in ordinary well waters is so rare that tests for them are not usually made. If any constituent is present in sufficient amount to be clearly perceptible to the taste, it is objectionable. Two parts per million of iron are unpalatable to many people, and even this small amount can cause trouble by discoloring washbowls and tubs and by producing rusty stains on clothes. Tea or coffee cannot be made satisfactorily with

water containing much iron because a black, inky compound is formed. Four or five parts of hydrogen sulphide are unpleasant to the taste, and this dissolved gas is objectionable also because it corrodes well strainers and other metal fittings. The amounts of silica and aluminium ordinarily present in well waters have no special significance in relation to domestic supply. Approximately 250 parts of chlorides make a water taste " salty," and less than that amount causes corrosion. Calcium and magnesium are chiefly responsible for what is known as the hardness of water. This undesirable quality is indicated by increased soap consumption, as calcium and magnesium unite with soap, forming insoluble curdy compounds with no cleansing value and preventing the formation of a lather until all of these two basic radicles has been precipitated. The use of soda ash to "break" hard waters, or to precipitate the calcium and magnesium, is common and effects saving in the cost of soap.

Purification of Water. Purification of water is the removal or reduction in amount of substances that render waters in their raw state unsuitable for use. It is practiced on a large scale with one or more of three objects in view: first, to render a supply safe and unobjectionable for drinking purposes; second, to reduce the amount of the mineral ingredients injurious to boilers; third, to remove substances injurious to the machinery or to the manufactured product in industrial processes. The largest purification plants in this country have been constructed for the purpose of producing potable waters without special attention to other possible uses, and some waters need no further treatment before being suitable for steaming and for general industrial purposes. But many other waters are hard, and increased appreciation of the value of good water has resulted in demand for the removal of the hardening constituents also. An excellent example of the result of such insistence is the recently installed plant at New Orleans, where hard, colored, turbid, sewage-polluted river water is brought up to practically all industrial and domestic standards of purity.

Removal of bacteria, especially those causing disease, and removal of turbidity, odor, taste, and iron are the principal requirements in purification of a municipal supply, elimination of bacteria and suspended matter being the most important. The common methods of effecting such purification are slow filtration through sand and rapid filtration after coagulation, both methods usually being combined with sedimentation. The first process is known as slow sand filtration and the second as mechanical filtration. The efficiency of such filters is measured primarily by the ratio between the number of bacteria in the applied water and the number in the effluent. This figure, stated in percentage of removal, should be as high as 98, and it often reaches 99.8 per cent with a carefully operated filter of either kind under normal conditions.

Removal of scale-forming and neutralization of corrosive constituents are the chief aims in preparing water for steam making, and two general

methods are employed, namely, cold chemical precipitation followed by sedimentation, and application of heat with or without chemicals usually followed by rapid filtration. The first process is carried on in cold-water softening plants and the second in feed-water heaters.

As can be understood from the remarks on pages 53 to 57 the requirements of the water supplies for industries are so varied that classification of purification methods used on them is difficult. Water properly prepared for domestic and boiler use is suitable for most industrial establishments, and it is more economical for small manufacturers in large cities to buy such water from public water companies if it can be obtained than to maintain private supplies and purification apparatus. It is usually cheaper, however, for large factories to be supplied from separate sources, not only because of saving in actual cost of water but also because of the opportunity thus afforded of procuring water specially adapted to the needs of the factory. The common methods of industrial water purification are those already mentioned or combinations of them modified to meet particular needs. Distilled water must be manufactured for use in a few industrial processes, notably the manufacture of ice by the can system, for which water practically free from all dissolved and suspended substances is necessary. In regions where the natural waters are of such quality as to be unfit for industrial use even after treatment by ordinary methods, supplies must be distilled. This is often effected by condensing steam from boilers. If large quantities are required the use of multiple-effect evaporators is advisable; though the cost of installing them is greater than that of boilers, the cost of operation is less because of the saving in fuel for heating.

Besides the four common systems of purification that have been cited several minor processes are used, sometimes alone but more frequently as adjuncts to filters or softeners. Surface waters may be screened through wooden or iron grids or through revolving wire screens to remove sticks and leaves before other treatment. Coarse suspended matter can be removed by rapid filtration through ground quartz or similar material in units of convenient size provided with arrangements for washing the filtering medium similar to those used in mechanical filters. (See page 63.) Very turbid river waters are first allowed to stand in sedimentation basins in order to reduce the cost of operating the filters by preliminary removal of part of the suspended solids. Supplies undesirable only because of their iron content are aerated by being sprayed into the air or by being allowed to trickle over rocks or falls, thus causing evaporation of carbonic acid and absorption of oxygen; this precipitates and oxidizes the iron in solution so that it can readily be removed by rapid filtration. Similar aeration is often employed for the purpose of evaporating and oxidizing dissolved gases that cause objectionable tastes and odors.

Disinfection by ozone, copper sulphate calcium hypochlorite, and other substances kills organisms that may cause disease or impart bad

odors and tastes. Purification of this character must be done with substances that destroy the objectionable organisms without making the water poisonous to animals. Such treatment is especially adapted for sewage [1], but it is also employed in connection with filtration of municipal supplies. Natural purification of water is accomplished largely through the biological processes mentioned by Hazen,[2] in which the organic matter is oxidized by serving as food for bacteria and objectionable organisms are destroyed by the production of conditions unfavorable to their existence. Action of this kind takes place in reservoirs and lakes, and it is also relied upon in many processes for the artificial purification of sewage.[3]

Slow Sand Filtration. Slow sand filtration consists in causing the water to pass downward through a layer of sand of such thickness and fineness that the requisite removal of suspended substances is accomplished. This filter is also called the continuous and the English filter. On the bottom of a water-tight basin commonly constructed of concrete, perforated tiles or pipes laid in the form of a grid are covered with a foot of gravel graded in size from 25 to 3 millimeters in diameter from bottom to top, and a layer of fine sand 3 to 4 feet in depth is put over the gravel, which serves only to support the sand. When water is applied on the surface it passes through the sand and the gravel, and flows away through the under-drain. The suspended solids, including bacteria, are removed by the sand, the action of which is rendered more efficient by the rapid formation of a mat of finely divided sediment on the surface. When this film has become so thick that filtration is unduly retarded, the water is allowed to subside below the surface and about half an inch of sand is removed, after which filtration is resumed. The sand thus taken off is washed to free it from the collected impurities, and it is replaced on the beds after they have been reduced by successive scrapings to a thickness of about 20 inches. As cleaning necessitates temporary withdrawal of filters from service they are divided into units of convenient size, usually half an acre each, so that the operation of the system may not be interrupted. Filters may be roofed and sodded; this facilitates cleaning by preventing the formation of ice, permits work on the filter beds in all kinds of weather, and inhibits algæ growths.

The foregoing are the essential features of a slow sand filter, but several adjuncts render this system of purification more efficient. A clear-water basin for the filtered supply, covered to prevent deterioration of the water, is provided in order that the varying rate of consumption may not affect the rate of filtration. Clarification of turbid water is

[1] Phelps, E. B., The Disinfection of Sewage and Sewage Filter Effluents. Water-Supply Paper, U. S. Geol. Survey, No. 229, 1909.

[2] Hazen, Allen, Clean Water and How to Get It. New York, 1907, p. 83.

[3] Winslow, C.-E. A., and Phelps, E. B., Investigations on the Purification of Boston Sewage with a History of the Sewage Disposal Problem. Water-Supply Paper, U. S. Geol. Survey, No. 185, 1906.

rendered more economical by allowing sedimentation for one to three days, during which period a large portion of the suspended matter is deposited, thus lengthening the time between sand scrapings. Another form of pretreatment is passage through roughing or preliminary filters consisting of beds of slag, sponge, or stone, through which the water flows at fifteen to twenty times the rate in sand filters, a very large proportion of the suspended matter being thus removed. Objectionable odors and tastes may be obviated by aeration before or after filtration. Killing the bacteria before filtration by means of ozone, chlorine, or other germicide is extensively practiced.

Slow sand filtration removes practically all the suspended matter and the bacteria. Color is only slightly reduced and the hardness is not changed. The process is especially adapted to waters low in color, suspended matter, and animal pollution. Very small particles of clay are not removed by these filters. It can readily be seen that the efficiency of this kind of filter depends largely on the character of the sand, as the ability to prevent the passage of suspended matter is governed by the size of the spaces between the sand particles. As it is obviously impracticable to procure sand with perfectly spherical grains of exactly the same diameter, the standards proposed by Hazen for comparing samples are generally used in this country.[1] These refer to the effective size and the uniformity coefficient of the sand as determined by mechanical analysis. The effective size is such that 10 per cent of the material is of smaller grains and 90 per cent is of larger grains than the size reported as the effective size. The uniformity coefficient is the ratio of the size of grain which has 60 per cent of the sample finer than itself to the size which has 10 per cent finer than itself. It is customary to use sand having an effective size between 0.2 and 0.4 millimeter averaging about 0.3 millimeter and with a uniformity coefficient between 1.7 and 4. The rate of filtration depends on the effective size, the uniformity coefficient, the thickness of the bed, the head of water, and the turbidity. Under ordinary conditions of operation in the United States the rate of filtration in slow sand filters preceded by sedimentation is from 2,000,000 to 4,000,000 gallons per acre per day.

Mechanical Filtration. The distinctive features of the mechanical process are the use of a coagulant and the high rate of filtration. The term "mechanical" is applied because of the contrivances for washing the filtering medium; the filter is known also as the American filter. The raw water during its entrance into the sedimentation basin, which is smaller than that used with slow sand filters, is treated with a definite proportion of some coagulant, which forms by its decomposition a gelatinous precipitate that unites and incloses the suspended material, including the bacteria, and absorbs the organic coloring matter. This combined

[1] Hazen, Allen, Some Physical Properties of Sands and Gravels, with Special Reference to Their Use in Filtration. Ann. Rept. Mass. State Board of Health, 1892, p. 541.

action destroys color and makes suspended particles larger and therefore more readily removable. Aluminium sulphate, the coagulant most commonly used, is decomposed, aluminium hydrate is precipitated, and the sulphate radicle remains in solution, replacing an equivalent amount of the carbonate, bicarbonate, or hydroxyl radicle. The natural alkalinity of many waters is sufficient to effect this reaction. According to Hazen [1] one part per million of ordinary aluminium sulphate should be allowed about 0.6 part of alkalinity expressed as $CaCO_3$ to insure complete decomposition. If the alkalinity is not sufficient, part of the aluminium sulphate remains in solution and good coagulation does not take place. Therefore lime or soda ash is added if the alkalinity is too low. The proper amount of aluminium sulphate to be used is determined by the amounts of color, organic matter, and suspended matter and by the fineness of the suspended matter, and is best ascertained by direct experimentation with the water to be purified. It may vary from 12 or 15 parts per million for water with 10 parts of suspended matter and a color of 30 to 25 or 30 parts for a water with a turbidity of 400 and a color of 80. Ferrous sulphate is sometimes used instead of aluminium sulphate as a coagulant; lime must always be added with it in order to bring about proper coagulation.

The water, after having been mixed with the coagulant, is allowed to stand three or four hours in the sedimentation basin, where a large proportion of the suspended particles is deposited. It is then passed rapidly through beds of sand or ground stone to remove the rest of the suspended matter. Sand with an effective size somewhat greater than that customary for continuous filters is used. Many filters now in use are built of wood or iron in cylindrical form 10 to 20 feet in diameter, and some are designed so that filtration can be hastened by pressure. The sand, 30 to 50 inches deep, rests on a metallic floor containing perforations large enough to allow ready issue of the water but small enough to prevent passage of sand grains. When the filter has become clogged the flow of water is reversed, filtered water being forced upward through the sand to wash it and to remove the impurities, which pass over the top of the filter with the wasted water. A revolving rake with long prongs projecting downward into the sand mixes it during washing and prevents it from becoming graded into spots of coarse or fine particles. In recently constructed works rectangular filters 300 to 1,300 sq.ft. in area have been built, and compressed air forced through the sand at intervals is used instead of a revolving rake for agitating the sand during washing. In conjunction with air agitation larger orifices in the strainers are being used and a layer of gravel is placed over the strainer pipes. The gravel is of such size that it prevents the entrance of sand and yet will not be displaced by the air and water passing through it during washing. The rate

[1] Hazen, Allen, Report of the Filtration Commission of the City of Pittsburg 1899, p. 57.

of filtration is from 80,000,000 to 180,000,000 gallons per acre per day. The time between washings is six to twelve hours, depending principally on the turbidity of the water applied to the filter, and 4 to 8 per cent of the filtered water is consumed in washing.

Mechanical filtration removes practically all suspended matter, reduces the color to an amount that is unobjectionable, and removes part of the dissolved iron under some conditions. The permanent hardness of the water is increased in proportion to the amount of sulphate added as aluminium sulphate, and if only enough lime to decompose the coagulant is added the total hardness is increased. If larger amounts of lime are added, however, the total hardness is reduced. If soda ash is used in place of lime the foaming constituents of the water are slightly increased. As this method of filtration is used almost entirely for river waters with fluctuating contents of suspended and dissolved matter, proper operation requires constant and intelligent attention. The chemicals in solutions of carefully determined strength should always be adjusted to the changing conditions of the water both in order to produce a properly purified effluent and in order to prevent waste of expensive materials.

Cold Water Softening. The principal objects of water softening are to remove the substances that cause incrustations in boilers, particularly calcium and magnesium, and to neutralize those that cause corrosion. Chemicals of known strength properly dissolved in water are added to the raw supply in such proportion as to precipitate all the dissolved constituents that can be economically removed by such treatment. The water is then allowed to stand long enough to permit the precipitate to settle, after which the clear effluent is drawn off, or filters of the rapid type may be used after partial sedimentation. The filters are thin beds of coke, sponge, excelsior, wool, or similar material, through which the water is passed at a very rapid rate to remove particles that have not subsided in the tanks. The water softeners on the market differ from each other only in the precipitant, in the filtering medium if one is used, and in the mechanism regulating the incorporation of the chemicals with the water. Installations may be of any size to suit consumption, and the process is frequently combined with mechanical filtration for purifying municipal water supplies, as in the recently erected plant at New Orleans.

Among the substances that have been proposed as precipitants are sodium carbonate, silicate, hydrate, fluoride, and phosphate, barium carbonate, oxide, and hydrate, and calcium oxide, but of these substances lime and soda ash are almost exclusively used on account of their excellent action and comparative cheapness. When soda ash and lime dissolved in water to form solutions of known strength are added to a water in proper proportion, free acids are neutralized, free carbon dioxide is removed, the bicarbonate radicle is decomposed, and iron, aluminium, and magnesium hydrates and calcium carbonate are precipitated. The four basic substances are removed to the extent of the solubility of these com-

pounds in water, and the calcium added as lime is also precipitated; in other words the scale-forming ingredients are removed.

According to Stabler,[1] therefore, lime should be added in quantity sufficient to provide hydroxide radicle (OH) to combine with the aluminium, magnesium, bicarbonate, and hydrogen radicles and with free carbon dioxide. If the amount of the carbonate radicle in the water with that formed by decomposition of the bicarbonate radicle and carbon dioxide is not sufficient to precipitate the calcium in the water and that added as lime, an additional quantity of carbonates must be provided by addition of soda ash. Expressed in formulas the required amounts of lime and soda ash are given by Stabler as:

$$C = 1.12\ Fe + 3.46\ Al + 2.56\ Mg + 30.96\ H + .51\ HCO_3 + 1.42\ CO_2,$$

$$D = 2.00\ Fe + 6.18\ Al + 2.78\ Ca + 4.58\ Mg + 55.44\ H - 1.86\ CO_3 - .92\ HCO_3.$$

The symbols represent the amounts of the different radicles in the water in parts per million, CO_2 being the free carbon dioxide and H the free acid expressed as hydrogen. C represents the required amount of 90 per cent lime and D the required amount of 95 per cent soda ash in parts per million.

The precipitate in settling takes with it the suspended matter and part of the silica and the organic matter; sodium, potassium, sulphates, and chlorides are left in solution, and the alkalies are increased in proportion to the quantity of soda ash that is added, that is, the foaming constituents are increased, and this is what fixes the maximum amount of incrustants that can be treated. (See page 53.) The minimum amount of incrustants in a treated water is determined by the solubility of the precipitated substances and by the completeness of the reaction between the added chemicals and the dissolved matter; it is about 90 parts per million. The sulphate radicle can be removed by using barium compounds, which precipitate barium sulphate, but the poisonous effect of even small amounts of barium is a great objection to its use. The chemicals should be very thoroughly mixed with the raw water and sufficient time should be allowed for complete reaction, which proceeds rather slowly, for otherwise precipitation will occur later in pipe lines or in boilers.

Feed-water Heating. Water heaters are designed primarily for the purpose of utilizing waste heat in stationary boiler plants by raising the temperature of the feed-water and thereby lessening the work of the boilers themselves, but some purification of water occurs in them and many heaters have been specially constructed to take advantage of that effect. The heat is derived from exhaust steam or from flue gases, and the heaters utilizing steam are either open, that is, operated at atmospheric pressure, or closed and operated at or near boiler pressure. In accordance with

[1] Stabler, Herman, *Eng. News*, Vol. LX, 1908, p. 355.

these three conditions, which result in distinct purifying effects, feed-water heaters are classified as open or closed or economizers, the last being those using flue gases. Open heaters are best adapted for removing large quantities of scale-forming material. The steam usually enters at the bottom of them and the water at the top, and intimate contact between the two is obtained by spraying the water or by allowing it to trickle over or to splash against plates. In this manner the water is quickly heated nearly to boiling temperature. Dissolved gases are expelled, the bicarbonate radicle is decomposed, and the iron, aluminium, part of the magnesium, and calcium equivalent to the carbonates after decomposition of the bicarbonates are precipitated as hydrates, oxides, or carbonates under varying conditions of temperature, pressure, and time. The precipitate agglomerates the particles of suspended matter and makes them more readily removable by sedimentation and filtration. The slowness with which the reactions take place and the presence of acid radicles other than carbonates to hold the bases in solution prevent complete removal of calcium and magnesium. The addition of soda ash in proper proportion, however, effects fairly complete precipitation of the alkaline earths and apparatus for constant introduction of this chemical in solution may be provided. After the precipitate has been formed the water passes through filters of burlap, excelsior, straw, hay, wool, coke, or similar material arranged in units that can readily be cleaned. Open heaters operated without a chemical precipitant remove substances that are soft and bulky and leave in the water the constituents that form hard scale; scale from water treated in such heaters is therefore not so great in amount, but is harder than that formed by the raw water.

In closed heaters the water is passed through metal tubes surrounded by steam at high pressure or around pipes in which steam circulates, and manholes or other openings are provided for cleaning the scale from the tubes. As the water is heated under pressure some precipitation takes place, but closed heaters are not so efficient in this respect as open heaters because there is no provision for the escape of the gases liberated from the water.

Economizers consist essentially of water tubes set in the flues leading from the furnaces. Facilities are provided for cleaning scale from the inside and soot from the outside of the tubes. As economizers are heated by flue gases, the water in the tubes can be heated under pressure to a much higher temperature than in open or closed heaters, and the boiler conditions described in the section on water for steam making are approximated. The precipitation of incrustants varies greatly with the normally fluctuating temperature of the flue gases.

IV

FUELS

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Definition. A fuel is a substance whose combustion in atmospheric oxygen can be utilized as a source of heat energy for commercial or domestic purposes.

Classification. Fuels are most conveniently considered as divided into three natural divisions, solid, liquid, and gaseous fuels.

Elementary Constituents. The two elements which contribute most to the heating power of fuel are carbon and hydrogen. Though other elements, such as sulphur, contribute somewhat to the formation of heat, the two mentioned above are by far the most important. That portion of the oxygen which occurs in the fuel as a partial oxidation product of some compound constituent thereof causes a loss in the heating value, as its presence means that a certain amount of the oxidation and heat development have been accomplished outside the furnace. Sulphur in small amounts is usually found in fuels. In large amounts it is undesirable, as it has a corrosive action and renders the fuel unfit for metallurgical uses. Nitrogen is usually an inert constituent, escaping uncombined during combustion. Silicon and phosphorus are also found in fuels, the latter being undesirable in metallurgical work. Together with the last two there is usually a considerable amount of mineral matter which is left after combustion as ash, and usually a certain amount of water which occurs free in the fuel. Ash is undesirable, as it dilutes the combustible matter of the fuel, causes an additional expense for its removal, and may interfere seriously with the use of the fuel because of its low fusion point and the consequent tendency to form clinker. Water is a direct loss of heat, as it dilutes the fuel, requires a large amount of heat for its evaporation, and by escaping up the flue at the temperature of the escaping gases, carries away a certain amount of heat.

Measurement of Temperature. In certain commercial operations it is necessary, in order to secure the best results, that the temperature be regulated between certain limits, and a knowledge of the temperature conditions becomes indispensable. The necessity of careful measurement and systematic regulation of the high temperatures obtained in many commercial operations has been recognized comparatively recently, and

it is well for the student to familiarize himself with methods for measuring high temperatures. The instruments used for this purpose are known as pyrometers.

Fig. 33 illustrates an instrument known as the Le Chatelier pyrometer. It consists of two wires of dissimilar metals melted together at one end, the other ends being connected with a needle galvanometer of comparatively high resistance. The deflection of the galvanometer needle is dependent on the temperature of the junction, and by providing the galvanometer with a suitable scale, the temperature can be read off directly from the instrument. The wires are generally made, one of platinum, the other of a 10 per cent alloy of platinum and rhodium, though couples of other metals are also used.

Fig. 33.

Fig. 34.

Fig. 34 illustrates a form of instrument known as the Wanner pyrometer. It is one of a class known as optical pyrometers, several of which

are on the market. Fig. 35 illustrates the construction of the instrument. Light from a 6-volt incandescent lamp used as a comparison, and from the object whose temperature is sought enters the slits U_1 and U_2, the two beams being rendered parallel by J and each dispersed into a continuous spectrum by R. C separates the dispersed light from both U_1 and U_2, into two beams polarized at right angles. The arrangement of the remain-

FIG. 35.

ing parts is such as to bring before the analyzer B an illuminated field, half of which is illuminated by red light from the spectrum of U_1, the other half by red light from the spectrum of U_2, the two halves being polarized at right angles to each other. If the analyzer is at an angle of 45° to the plane of polarization of each beam, and U_1 and U_2 are equally illuminated, the field is uniformly bright. If they are unequally illuminated one-half of the field will appear brighter, and they are equalized by turning B, which carries a scale that can be interpreted in terms of degrees of temperature.

Another form of pyrometer, known as the Féry, is also direct reading, and is constructed by focusing the radiations from the object by either a lens or a concave mirror on a delicate thermo-couple.

Such instruments as the optical pyrometers are the only ones which fulfill all requirements for much of the high-temperature measurements to be made in commercial work.

Heat of Combustion. The heat of combustion of a substance is the number of calories produced by the complete oxidation of one gram of it. As applied to fuels, it is called the calorific value or heating power of the fuel. The calorific value is one of the most important points to be decided in the purchase of a fuel. Having decided the character of fuel best adapted to the purpose for which the purchase is to be made, the remaining point of chief consideration is the calorific value, which is determined by means of a calorimeter. Solids and non-volatile liquids are usually burned in a heavy steel bomb in an atmosphere of oxygen under a pressure of about 25 atmospheres.

FIG. 36.

[1] Bulletin No. 2, Bureau of Standards, Washington, D. C.

Fig. 35 illustrates one of the standard forms of this kind of instrument, known as the Mahler calorimeter. It consists of the porcelain or platinum-lined steel bomb *A*, with a tightly fitting top *B*, which carries the connection *R* for admitting oxygen under pressure, the platinum vessel *C*, into which the substance is weighed, and the terminals for igniting the charge, one of which, *E*, is insulated from the top *B*. The substance is ignited by connecting a piece of fine iron wire beween the terminals, having the wire in contact with the charge. When a current is passed through the wire it is heated to incandescence, and both it and the charge are completely oxidized. The calorimeter is immersed in water contained in a vessel protected by non-conducting material from temperature changes. The temperature of the water before and after the experiment, the amount of water and the water equivalent of the calorimeter being known, the total amount of heat liberated by the action is obtained.

The calorific value of gaseous fuels is determined by burning a measured volume of the gas in the atmosphere and determining the amount of heat liberated. Fig. 36 shows a longitudinal and transverse section of a reliable form of gas calorimeter, known as the Junker calorimeter. It is a double-wall copper vessel, so arranged that a steady stream of cold water circulates between the two walls. This stream of water is kept constant by the constant-level devices placed at the entrance to, and the exit from the instrument. The gas, previously measured in an accurate gas meter, is burned in the special burner placed in the combustion chamber of the calorimeter. The heated air and products of combustion ascend to the top of the combustion chamber, and from there descend through two sets of vertical copper tubes which are surrounded by the water that

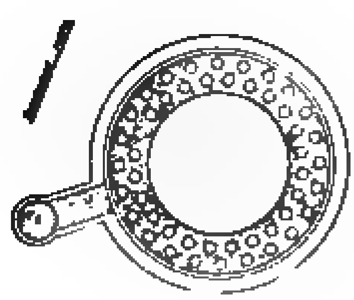


Fig. 36

circulates between the two walls of the instrument. The arrangement of this water jacket and the copper tubes through which the heated gases pass is best seen from the horizontal cross-section of the calorimeter shown below in Fig. 36. During the passage of the heated gases through the water-cooled tubes the heat is taken up by the water and the temperature of the water in its passage through the instrument is somewhat increased. Before beginning a determination the flow of water is started through the instrument, the burner lighted and the thermometer readings allowed to become steady. In this way the water passing through the calorimeter during the burning of a known volume of gas contains all the heat resulting from the combustion of this gas. This water is collected and weighed, the increase in temperature of the water is obtained by the difference in the readings of the two thermometers, and knowing the volume of gas burned from the readings of the meter, all the data have been obtained for calculating the heating power of the gas per unit volume.

The heating power of the gas can be calculated from the chemical composition and heats of combustion of its constituents. But the time required to obtain an accurate analysis is greater than that required by the above determination, and it offers no advantages over the direct determination.

Solid Fuels

Wood. Wood is composed principally of cellulose and ligno-cellulose in about equal quantities, together with gums, resins, a variable amount of water, and inorganic matter left as ash when the wood burns. Cellulose has the composition ($C_6H_{10}O_5$) and is the principal constituent of the cell membranes of young plants. The formula above serves only to give the percentage of the constituents, the molecule being very complex.

Ligno-cellulose is the substance with which the cellulose of young plants becomes incrusted as it grows old, and becomes woody fiber. It is not a carbohydrate, and little is known of its chemical nature.

Wood has a low calorific value, varying from 3000 to 3500 calories, and contains a considerable amount of moisture, the amount depending on the kind of wood, the season in which it is cut, and the extent it has been allowed to dry, being rarely less than 18 per cent.

Wood is of little value as a fuel, as it has a low calorific value, and is too expensive. But it is sometimes used on account of its cleanliness and small amount of ash formed.

Below is given a table [1] containing the results of the analysis of seven different kinds of wood together with their calorific values:

[1] Jour. Chem. Soc., Vol. XLVI, p. 477 (1884).

	C	H_2	N_2	O_2	Ash	Calories
Oak	50.16	6.02	0.09	43.36	0.37	4620
Ash	49.18	6.27	0.07	43.91	0.57	4711
Elm	48.99	6.20	0.06	44.25	0.50	4728
Beech	49.06	6.11	0.09	44.17	0.57	4774
Birch	48.88	6.06	0.10	44.67	0.29	4771
Fir	50.36	5.92	0.05	43.39	0.28	5035
Pine	50.31	6.20	6.04	43.08	0.37	5085

Peat. There is no doubt that peat represents a comparatively early stage in the transformation which vegetable matter undergoes when sufficiently protected to prevent its complete oxidation, as in many localities it is possible to observe the transition from the vegetable matter covering the ground to the underlying peat in various stages of formation. In the upper portions the vegetable matter is easily discernible, while at the bottom, most, if not all, visible signs of plant remains disappear. The formation of peat occurs in bogs or swamps where sufficient vegetable matter accumulates to give rise to the formation. The deposit from each year's growth, such as mosses, grasses, leaves, branches and trunks of trees fall and are partially protected by the water from complete decomposition. The action of organisms and atmospheric oxygen transforms this material first into a loose brown substance, finally, with the aid of pressure from above, into a brown or black peat.

Little is known of the chemical compounds composing peat. Some solvents and solutions of alkalies dissolve considerable amounts of organic matter of a complex character from peat, but the substances obtained from these solutions are probably impure.

Peat has long been used as a fuel, and in northern and western Europe, and in Ireland (where peat bogs are said to cover one-tenth of the total area) it has been extensively used. Peat bogs are also widely distributed in this country and Canada.

The recent peats are usually brown in color and approach wood in chemical composition, containing less oxygen and hydrogen and more carbon. The oldest peats are usually dark in color, and the percentage of carbon is greater than in recently formed peats.

Peat has a higher calorific value than wood, varying from 3500 to 5000 calories. As it is cut from the ground it contains a large amount of water, often as much as 90 per cent of its weight. If the blocks are left to dry under cover in the air this is greatly reduced. The difficulty of freeing it from this water is one of the drawbacks to its use. By application of pressure much of it can be expelled, but it still contains a considerable amount on account of its jelly-like character. A recent observation [1] that this jelly-like character is destroyed by heating it to 150° after which

[1] Engineering, 87, p. 737.

the water can be expelled by pressure, may assist in the solution of this difficulty.

The following analyses[1] give an idea of its composition and the progressive increase in carbon and loss of oxygen taking place during the peat formation:

	1	2	3	4	5	6	7
C	49.88	50.33	50.86	59.71	59.70	59.71	62.54
H	6.54	5.99	5.80	5.27	5.70	5.27	6.81
O	42.42	42.63	42.57	32.07	33.04	32.07	29.24
N	1.16	1.05	0.77	2.95	1.56	2.95	1.41
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

1. Sphagnum, the chief peat-forming plant.
2. Light peat near surface.
3. Light peat.
4. Moderately light peat.
5. Black peat.
6. Black peat.
7. Heavy brown peat.

Peat is frequently formed into briquettes, when it makes an excellent fuel for domestic uses, as it burns with a bright cheerful flame and without much smoke. The following table gives the analyses of samples of peat from this country.

ANALYSES OF PEAT (AIR DRIED)

Locality	Florida	Michigan	New York	
Moisture	10.17	14.22	7.09	
Volatile Matter	54.93	49.11	56.09	
Fixed Carbon	28.98	24.83	24.83	23.97
Ash	5.92	11.84	12.85	
Calories	5249	3979	4275	

Lignite. Lignite or brown coal are names applied to the substances which represent the next stage to peat in the transformation of vegetable matter into coal. The distinction of lignite from peat on the one side and bituminous coal on the other is not sharp, as the transition from one to the other is gradual. Chemically, lignite seems to be more closely related to peat than to bituminous coal and, as with peat, it is found that certain solvents and solutions of alkalies dissolve considerable organic matter of a complex character from lignites. The evidences of vegetable origin are not usually distinct in lignites, though when properly treated, microscopic examination is usually able to show the remains of plant structure. In general, lignite is denser, darker in color, and contains more carbon than peat. It contains about 35 per cent of water, and on air-drying this falls to about 15 per cent. Its calorific value varies

[1] Jour. Prakt. Chem., vol. 92, p. 65.

from 4000 to 6500 calories. The amount of ash varies greatly, but should not exceed 10 to 15 per cent.

On account of the difficulties encountered in shipping and storing lignite, its formation into briquettes has been practiced to a considerable extent, especially in Germany. In this country the necessity for using such fuels has not been greatly felt, and the operation of briquetting such fuel is here in its beginning. This question will be mentioned later in connection with bituminous coal.

The following table gives the analysis of some samples of lignite from this country:

Locality	N. Dakota	Texas	California	Wyoming	Montana
Moisture	16.70	22.48	18.51	17.69	9.05
Volatile Matter	37.10	31.36	35.33	37.96	36.70
Fixed Carbon	39.49	26.73	30.67	39.56	43.03
Ash	6.71	19.43	15.49	4.79	11.22

Bituminous Coal. The next stage in the formation of coal is represented by bituminous coal, by far the most important of all the classes of fuels. The division of bituminous coals from lignites is more sharply defined than that of lignites from peats, but still the transition is gradual.

The origin of coal is swamp flora laid down when the growth of vegetable matter was far more luxuriant than now, and which in earlier geologic ages has passed through successive stages which are represented now by peat bogs and beds of lignite.

The properties of bituminous coals differ widely. The amount of volatile matter varies from 15 to 50 per cent, the amount of ash from 2 to 20 per cent, but the most marked differences are observed in the coal substance when heated. The differences are noticed in the characters of both the volatile matter and the residue or coke. Some, when heated fuse together to a compact mass, and if heated sufficiently leave behind a firm, solid mass composed principally of carbon and the ash of the coal. Such coals are said to be caking coals. Non-caking coals do not fuse and the mass left behind when such coals are heated coheres only slightly or not at all.

Coals are frequently changed, after mining, by the absorption of oxygen and the loss of some of their combustible constituents, and on long standing their heating power is materially changed, some, even losing their caking power. Frequently, this absorption of oxygen is so rapid and accompanied with the evolution of so much heat that when large amounts are stored in one pile the temperature gradually rises until spontaneous combustion ensues.

To overcome some of these difficulties and to utilize those portions of the fuel which unavoidably go to waste around the mine, finely divided

coal is frequently mixed with pitch or tar, and compressed while hot into molds. These briquettes are less bulky, less likely to deteriorate and to undergo spontaneous combustion, and can be fired more efficiently than the raw coal. Where it is necessary to keep large stores of coal on hand, these advantages are sufficient to justify the operation of briquetting. The practice of briquetting coal and lignite is more common in Germany than in this country. In 1906, 14,500,851 tons of briquettes were made in Germany, including those made from lignites.

One of the chief objections to the burning of bituminous coals is the production of smoke during combustion. It is doubtful if this can be prevented by any means which involves the introduction of fresh coal directly into the fire. Mechanical stokers, such as illustrated in Figs. 37 and 38, are designed to bring the fuel into the fire slowly, and at a regular rate. In Fig. 37 this is accomplished by a rocking motion of the grate bars

Fig. 37.

which are set at the proper angle, and in Fig. 38 by the forward motion of the grate bars arranged as a continuous chain. In this way the volatile matter is expelled gradually and mixed with sufficient oxygen for its combustion, the result being that less smoke is produced, the fire kept in a more uniform condition than is possible by hand firing, and at the same time the fuel is consumed more efficiently.

	Moisture.	Volatile Combustible.	Fixed Carbon.	Ash.	Sulphur.	Calories.
West Virginia.............	0.80	32.24	62.33	4.63	1.65	8167
Indiana..................	4.93	35.28	50.82	8.97	1.00	6979
New Mexico...	1 36	33 77	52.31	12.56	1.21	7173
Kentucky	1 16	30.81	61.01	7.02	0.58	7785
West Virginia.......	0.47	14.80	81.59	3.14	0.52	8447
West Virginia.............	0.60	15 48	79.64	4.28	0 46	8306
Illinois...................	4 00	28.86	58.56	8.58	0.95	[illegible]
Illinois...................	7.67	28 96	57 69	5 68	0.48	6958
Pennsylvania	1.47	27.63	63.66	7.24	0.97	7875
Pennsylvania	0.71	16.59	76.83	5.87	0.98	8296

Analyses made in the fuel-testing laboratory of the Technologic Branch, U. S. Geological Survey.

FIG. 38.

Anthracite. In composition the anthracite coals approximate the final stage in the carbonization of vegetable matter. On one side of the anthracite we have bituminous coals separated by the semi-anthracites, and on the other side the anthracites approach graphite. As indicated above, anthracites contain a large amount of fixed carbon as compared with their content of volatile matter. They are denser than bituminous coals, have a conchoidal fracture, and a high kindling temperature. Anthracite is used largely for metallurgical work, for the manufacture of producer and water gases, and for domestic purposes. As it has little volatile matter, and burns with a non-luminous flame, it is well adapted to these purposes.

Below are the analyses[1] of some semi-anthracite and anthracite coals of this country:

Locality	Arkansas	Rhode Island	Indian Ter.	Virginia	Pennsylvania
Moisture	5.19	2.41	5.11	4.80	3.33
Volatile Matter	10.49	4.92	13.65	10.12	3.27
Fixed Carbon	70.31	73.61	73.21	67.05	84.28
Ash	14.01	19.06	8.03	18.03	9.13
Sulphur	2.05	0.07	1.18	0.63	
Calorific Value	6922	6109	7590	6645	7417

Charcoal. Charcoal is made from wood by two methods. By the first, wood is converted into charcoal by what is called the charring process. This consists of piling the wood into large circular heaps, leaving horizontal flues near the bottom and a vertical flue at the center for the escape of the evolved gases and covering over the whole, except for these points of ventilation, with powdered charcoal, earth and turf. At the points of ventilation the wood burns, the area of the combustion depending on the drafts, and the heat produced by the burning at these points suffices to raise the temperature of the whole mass to the point where most of the volatile matter of the wood is expelled. When all the volatile matter has been driven off and the escaping gases cease to burn with a luminous flame, the draft holes are covered and the operation stopped. By this process air-dried wood yields about 25 per cent of charcoal, but all the volatile matter is lost.

By the second method of preparing charcoal provision is made for the recovery of these by-products, which consist of combustible gases, wood alcohol, organic acids, acetone and tar. For the details of this process see Chapter XXIV. The operation consists in the destructive distillation of wood from closed vessels, the charcoal remaining in the retort. For the production of charcoal for certain purposes these retorts are heated by means of super-heated steam.

Charcoal is quite porous and brittle and retains the shape of the wood, though the pieces are only about three-fourths the size of that of the wood. It still contains traces of volatile matter from which it is impossible to free it, and the ash-forming constituents of the wood. It burns with little flame, contains little sulphur and phosphorus, a low amount of ash, and has been extensively used in metallurgical work, especially for the production of the finer grades of iron and steel. Its calorific value is about 7000 calories. The porosity depends on the character of the wood used in preparing it, some giving a denser product than others. It possesses the peculiar property of condensing many gases before they reach their point of liquefaction, and of abstracting coloring matter from

[1] Analyses made by U. S. Bureau of Mines.

solutions. This power of absorbing materials is frequently utilized to purify solutions from tarry materials and coloring matter. Because of the great tendency of charcoal to hold back small amounts of other substances perfectly pure amorphous carbon is unknown.

Coke. Coke is the residue left after the destructive distillation of coal, and is composed principally of carbon and the ash-forming constituents of the coal from which it was formed.

The production of coke was at first carried out in much the same way that charcoal is obtained from wood in charcoal kilns, the bee-hive oven of to-day, in which most of the coke produced in this country is made, is a development of this method.

Fig. 39 illustrates the bee-hive oven as used in this country. It is simply a dome-shaped enclosure built of fire brick, 12 ft. in diameter, 7 ft. high, with an opening at the top for charging and for the escape of the products of combustion and volatile matter formed during the operation, and a door at the side through which the coke is withdrawn, usually by hand, at the end of the operation. This door is built up with firebricks during the process, except at its top above the level of the charge. In this way five to six tons of coal are coked at each charge, and the time required from forty-eight to seventy-two hours, yielding from 60 to 65 per cent of coke. The operation is brought to an end by quenching the fire in the oven with a stream of water, after which the coke is withdrawn. These ovens are usually built together in one or two rows, with a track on top to bring up the coal.

FIG. 39.

As seen from the above description, the burning of a part of the coal furnishes the heat necessary for coking the remainder, and the volatile matter of the coal is either burned or turned into the air.

Numerous forms of ovens have been designed to collect these products and use them. These so-called by-products consist of combustible gases,

various organic compounds, compounds of nitrogen including ammonia and tar.

Figs. 40, 41 and 42 are illustrations of two types of by-product coke

Fig. 40.

ovens which are used considerably in this country and will serve to illustrate the operation.

The Otto-Hoffmann type of oven is shown in transverse and longi-

Fig 41.

tudinal sections in Figs. 40 and 41. The coal is charged through *d* into the coking chambers *D* beneath. These are long, narrow retorts of fire-

brick construction placed side by side, usually in groups of fifty. In the walls separating the retorts are the vertical flues *f*, in which the gas evolved in coking previous charges is returned from the condensing house and burned to furnish the heat for coking the charge. The retorts are about 33 ft. long, 6½ ft. high and 20 ins. wide, closed at each end by an iron door which is raised and lowered electrically, and during the coking process luted with fire-clay. The air for the combustion of the gas passes through the checker work *R*, made of refractory material, which, as we will see, is highly heated, the gas entering at the burner *B*. The burning gases pass along the horizontal flue F_1, and up each of the vertical flues *f* of one-half of the retort wall to the upper horizontal flue F^1, then down the remaining vertical flues *f* of the second half of the wall to a similar horizontal flue F_2, situated beneath the coking chamber *D*, then out through the second chamber or regenerator *R′* filled with refractory checker work, where the heat of the escaping gases is abstracted by heating up the checker work to incandescence. After a certain length of time, when *R′* has been heated and *R* cooled, the currents of air and gas are reversed through the flues, the air entering through *R′* and the gas through another burner at the other end of the retort. The volatile products escape from *D* through the uptake pipes, provided with valves, and pass into the common main *G* at a high temperature, and are gradually cooled in the iron pipes, depositing some of the condensable portions, the remainder being subsequently removed in the condensing house.

After the completion of the coking process, the charge is removed by a steam or electrically operated pusher, which pushes the whole charge of the retort out on the opposite side, where it is rapidly cooled by a stream of water.

The time required for coking a charge in this type of oven is about twenty-four hours, yielding about 70 per cent of coke.

In the Semet-Solvay type of by-product oven, shown in Fig. 42, the coking chamber *D* is somewhat similar to that of the Otto-Hoffmann oven above. They are built in sets of thirty or forty, are 35 ft. long, 7½ ft. high and 16½ ins. wide.

The coal is charged through *d* into the coking chamber *D*, the volatile products escaping through *g* into the common main *G*. The flues *f*, built in the walls of the ovens, are in this type five in number and arranged horizontally. The gas returned from the condensing house is delivered at the four burners *B*, and mixes with preheated air delivered from beneath the oven. The current of burning gases is from the top flue downward through each of the others, fresh gas burning at each of the burners during their downward course. The gases from the flues in each wall of the chamber pass into a single flue beneath *D*, thence into a series of channels with thin walls where the air passing to the burners is preheated, as stated above. The flue gases are subsequently passed through water-tube boilers, and their remaining heat used to generate steam for power

purposes. A charge of from seven to nine tons of coal can be coked in these ovens in about twenty-four hours.

Coke is also obtained as a by-product in the manufacture of coal gas, which will be mentioned later. But the coke obtained in this way is soft and unfit for metallurgical purposes, and is partly consumed in the producer used to heat the retorts, and for domestic purposes.

During the coking process the coal fuses and the escape of the gases formed by the destructive distillation of the coal leaves the residue or coke full of cavities, the walls of which are quite hard. This cellular structure is very advantageous, as the coke to be of service for metallurgical work must be sufficiently strong to sustain the charge above without crushing, and at the same time must be porous. It has a silvery

FIG. 42.

white luster, a metallic ring when struck and is infusible. It burns without smoke and has a calorific value of 7600 to 8100 calories. All of the ash of the coal and ordinarily about half of the sulphur remain in the coke, and it is frequently necessary to wash the coal to remove portions of these constituents in order to make a serviceable quality of coke. The phosphorus of the coal is all found in the coke. Besides these, there is a considerable amount of nitrogen and water, and small amounts of hydrogen and oxygen which cannot be driven off by heat. Some coals, which do not yield a good quality of coke, can be mixed to advantage with a good coking coal.

The great use of coke is for metallurgical purposes, but a great deal is used in gas producers, on railroad engines and for domestic purposes.

The objection to the use of coke made in by-product ovens seems to have been without foundation, and the relative amount of coke made in the by-product ovens has increased steadily and rapidly. About 16.5 per cent of the coke made in this country is made in the by-product ovens, and in Europe these ovens are in general use. It seems that in a short time most of the coke made in this country will be made in this way, the increase being limited only by the demand for the by-products.

Liquid Fuels. The only liquid substances which have any extended use as fuels are crude petroleum and various products obtained by its fractional distillation; as petroleum spirit, lamp oil, and the residue or "residuum" left in the retort after the distillation of the lubricating oils. Tars obtained as by-products in other industries are sometimes burned as fuels when a more remunerative market is not available, but they are too expensive for this purpose. The objection of expensiveness applies also to alcohol at present, but as it possesses certain advantages as a fuel, and its production is subject to our control, it is possible that it may assume more importance in the future if it can be produced more cheaply.

Petroleum. Petroleum is widely distributed, but 86 per cent of the world's output comes from this country and Russia; the United States producing 63 per cent and Russia 23 per cent of the total.[1] In this country the Pennsylvania fields have been most prominent, and it was here that oil was first obtained by systematic borings. Besides Pennsylvania, many other states have become oil producing states, as Ohio, Texas, and California.

In using crude petroleum as a fuel the greatest objection is that the volatile portions will escape and mix with air and form an explosive mixture, as it requires only small amounts to form an explosive mixture with air. But it is only necessary to remove these by distillation to avoid such danger.

In burning crude oil in furnaces it is first converted into a very fine spray by means of special burners, and the spray directed against refractory material, which, becoming incandescent, transmits much heat to the boiler by radiation, and it also effects better combustion. These burners are operated in two ways. In the first, the oil is "atomized" by forcing it under pressure through burners so constructed as to send the oil into the furnace in a sheet of finest spray. By the second the same disintegration of the oil is accomplished by a jet of steam. The objection to the second method is that a large amount of steam is consumed, and the flame is cooled down at the point where the combustion should be most rapid, and, while steam is effective in securing the combustion of the last portions and preventing the formation of smoke, it can be best introduced later in the flame and in smaller amounts.

Several advantages are obtained by using petroleum as a fuel. It has a high calorific value, from 10,000 to 10,500 calories, is more uniform than coal, is easily regulated to secure complete combustion and the rate of combustion can be changed by merely turning the valve admitting the fuel. It does not deteriorate if kept in covered tanks, and no spontaneous combustion occurs. It requires a small fraction of the number of stokers required to burn coal, gives no ashes, cinders or smoke when properly burned, and is easily transferred at sea through flexible hose by pumps.

[1] The Production of Petroleum in 1907. U. S. Geological Survey.

Still the output is so small when the total amount of fuel consumed is considered, and the supply so uncertain, that it seems that petroleum as a fuel must remain an adjunct except near the sources of supply and for certain special purposes such as on fast ocean-going ships, for use in navies, and to assist in meeting sudden demands on powerhouses of a temporary character.

Gaseous Fuels. When the products of combustion of solid fuel are allowed to pass through a bed of incandescent carbon they are partially reduced, and can be ignited on their escape. The pale blue flame often seen burning at the top of an open grate fire is an illustration. And if the fuel bed were sufficiently thick and hot enough to reduce most of the carbon dioxide and water formed at the bottom of the grate, and provision made for collecting the gas, we should have a sample of producer gas.

Producer gas is, then, the combustible gas obtained by the burning of solid fuel with a restricted supply of air, or with air and steam together in such a way that there is subsequent reduction of the products of combustion and the steam by incandescent carbon. When air alone is used, the gas is called " air gas." When steam is blown in along with the air the gas obtained is called " semi-water gas." By the action of steam alone on heated carbon the product is " water gas."

Whenever carbon burns the first product of the reaction is carbon dioxide according to Eq. (1) $C+2O=CO_2+96960$ calories. If the supply of oxygen is limited and there is sufficient contact of the gases with the carbon the temperature increases until the carbon dioxide first formed is partially reduced according to Eq. (2) $CO_2+C\rightleftarrows 2CO-38960$ calories. Of the 96960 calories developed in the formation of the gram-molecule of carbon dioxide according to Eq. (1), 38960 calories are consumed in the second reaction and stored up as chemical energy in the carbon monoxide formed, and 58,000 calories liberated. As two gram-molecules of carbon monoxide are formed in Eq. (2), the 58,000 calories liberated constitute about 30 per cent of the total heat of combustion of the two gram-molecules of carbon which are present in the combustible gas formed, when burned according to Eq. (1). In other words, by this method of converting solid carbon into carbon monoxide, about 30 per cent of the heat of combustion of the carbon is liberated in the producer, even if the reaction according to Eq. (2) is complete, which is never the case, for the reaction is, as represented, reversible, and for every temperature there is a definite composition of the gas mixture which is in equilibrium with carbon at that temperature. The extent to which the action approaches equilibrium depends on the velocity of the action and the time and extent of contact of the gases with the heated carbon. This heat evolved in the producer need not all be lost, as the gases may be used while much of this heat is contained in them, or it may be used to preheat the air and steam put into the producer, but the loss will still be about 20 per cent of the heat of combustion of the carbon.

Producer gas has the lowest calorific value of any gaseous fuel, and the temperature of its flame is the lowest of any, yet it is the cheapest artificial gas per unit of heat. It has become of great commercial advantage, as nearly any kind of solid fuel can be converted into a gaseous fuel in the producer. Although about 20 per cent of the total heat of combustion of the fuel is lost in the producer, the remainder can be used so efficiently that the loss is more than retrieved. Its use in connection with the gas engine is an efficient means of power generation. With care it can be burned with a small excess of air, and complete combustion secured, causing a smaller amount of heat to be carried away by the escaping gases.

It is finding application in commercial work of many kinds where a gas of high calorific value is not required.

Siemens' Regenerative Furnace. The method used in connection with the Otto-Hoffmann oven above, for recovering the heat from the flue gases is known as the regenerative system. Fig. 43 is an illustration

FIG. 43.

of this type of furnace, which was first worked out by Siemens in connection with his gas producer, and known as the Siemens "regenerative" furnace. Beneath the furnace proper, *A*, are four chambers, *B*, *C*, *D*, and *E*, filled loosely with firebrick. The gas and air enter through *B* and *C*, and after burning pass out through *D* and *E*. After the interior of *D* and *E* is highly heated the direction of the gases is reversed, the gas and air entering through *D* and *E*, where they are highly heated before burning, and escape through *A* and *B*. Various methods have been worked out for the recovery of the heat contained

in the gases which escape hot after the completion of an operation. This is illustrated in the Otto-Hoffmann and Semet-Solvay coke ovens above, and in connection with gas producers it is a matter of considerable importance to use as much as possible of the heat of the escaping gases to preheat the air and steam introduced into the producer.

Water Gas. Steam is usually forced into the gas producer along with air to overcome practical difficulties encountered in operating the producer with air alone, and at the same time to increase the calorific value of the gas. As the action of steam on carbon is accompanied with an absorption of heat, it is necessary to supply heat to continue the operation. The production of "semi-water gas" is made a continuous operation by the heat generated by the action of the oxygen of the air on the fuel in the producer. By separating the two operations taking place in the formation of "semi-water gas," and collecting the resulting gases separately, we would obtain "air gas" and "water gas." The intermittent operation of the producer with air and steam is the usual method of preparing water gas. The producer is operated a few minutes with air until the temperature is sufficiently high, when steam is passed in until the temperature falls too low to produce a gas of high calorific value.

The action of steam on highly heated carbon results in the formation of carbon dioxide, hydrogen, and carbon monoxide in proportions varying with conditions. It is customary to express the action by the following two equations:

$$(1) \quad 2H_2O+C=CO_2+2H_2-18340$$
$$(2) \quad H_2O+C=CO+H_2-28650.$$

At low temperatures the reaction is mostly according to Eq. (1) while at more elevated temperatures, according to Eq. (2).

As the gases formed by these two reactions are capable of reacting according to Eq. (3) $CO_2+2H \rightleftarrows CO+H_2O-9310$, and since equilibrium is obtained more readily between gases than between a solid and a gas, the composition of the water gas will tend to approach the condition of equilibrium according to this equation.

The producer used to generate water gas does not differ greatly from the ordinary gas producer. The first successful water gas plant was worked out by Lowe in 1874. Fig. 44 is an illustration of such a plant, Air enters at *E* and the "air gas" formed during this operation passes out at *F*, where it meets with additional air at *G* and is burned. *B* and *C* are two chambers filled with checker work, which is highly heated by the burning gases. The air currents are then stopped and steam passed in at the top of *C* and enters *A* highly heated. It is decomposed by the incandescent carbon and the gas formed passes out at *K*.

For illuminating purposes, water gas which burns with a non-luminous flame is passed over highly heated surfaces over which a slow

stream of petroleum is allowed to flow. The products of decomposition of the petroleum mixing with "water gas" contribute the desired illuminants. (See Chapter XXI.)

By having a thin fuel bed it is possible to operate during the introduction of air in such a way that practically no carbon monoxide is produced, and the total heat of combustion of the carbon consumed is liberated in the producer. The time required for the operation with

Fig. 44.

the air blast is much reduced in this way. The composition of water gas is about as follows:

Hydrogen	51.5
Carbon monoxide	41.0
Methane	0.1
Carbon dioxide	4.0
Nitrogen	3.4
	100.0

It is composed almost entirely of combustible gases and has a calorific value much higher than producer gas. The presence of such large amounts of carbon monoxide, which is highly poisonous and without odor, constitutes a danger in its use.

Coal Gas. Coal gas is made by the destructive distillation of coal in fireclay retorts of special construction. Fig. 46 is a transverse section through a bench of such retorts. They are mounted above a gas producer which furnishes the gas with which the retorts are heated. Above is a fireclay arch. Each retort effects the distillation of a charge of about 400 lbs. in four hours. The gas escapes through a cast-iron mouthpiece which closes the open end of the retort and into a common main, where the

Fig. 45.

opening of each tube is water sealed to prevent back pressure when the retort is opened.

The composition of the gas varies with the kind of coal used and the conditions during distillation. These cause greater change in the illuminating power than in the calorific value. It burns with a bright, often sooty flame, and as it is composed almost entirely of combustible gases it has a high calorific value. The coke left in the retort is of inferior quality because of the method used to effect distillation and the character of the coal necessary to form a good quality of gas.

It is used principally for illuminating purposes, and on account of its high calorific value, it is used to some extent where a great deal of fuel is not needed. For further particulars see Chapter XXI.

The following [1] is an average composition of coal gas:

Hydrogen	48.0
Carbon monoxide	8.0
Methane	36.0
Unsaturated hydrocarbons	3.8
Nitrogen	4.2

Oil Gas. Oil gas is made by the destructive distillation of petroleums. It is somewhat similar to coal gas, and contains a considerable amount of unsaturated hydrocarbons which imparts luminosity to the flame.

Natural Gas. Natural gas occurs ready, formed in the earth, and in the oil regions of Pennslyvania and Russia it is found in enormous quantities. It always accompanies petroleum, and their origins are closely connected. It is frequently confined under great pressure, and when borings are made through the overlying strata its escape is at times beyond control. While it always accompanies petroleum, it is sometimes found alone.

As it is composed almost entirely of combustible gases, its calorific value is very high. The natural gas of this country burns with a slightly luminous flame, and has a higher kindling point than other gaseous fuels. When it is properly burned it is an excellent fuel because of its high calorific value and practically smokeless flame.

The composition of natural gas varies according to the locality, that from any one district remaining quite uniform in composition.

[1] J.S.C. I., 1888, p. 20.

V

PRODUCER GAS

OSKAR NAGEL

Consulting Chemical Engineer, New York City

The Producer. The producer is a simple and efficient apparatus for the manufacture of a cheap industrial gas. Other important advantages of this apparatus and its application are: smokeless combustion of great uniformity, exact regulability of the fire and heat, and the attainment of very high temperatures by preheating the air of gasification and combustion. By working with an excess of air or gas, respectively, an oxidizing or reducing flame is produced. Finally the combination of the various fireplaces into one central station and the saving effected in the cost of transportation of fuel and ashes are factors which should by no means be underestimated.

The Construction of Gas Producers. The first and oldest type of producer is that which has been developed from the blast furnace and is a vertical shaft in which the fuel moves downward, while the air and the gas travel in the opposite way. The gas formed passes through the green fuel, carrying along water and volatile matters. The shaft is built of firebricks and surrounded by a wrought-iron shell. The tops of the producers are sometimes made of an arch of firebricks, but frequently only provided with water-cooled covers made of iron. Cast steel is also sometimes used for the parts that are exposed to considerable heat. The shaft is generally circular, sometimes, however, square. The walls are mostly vertical, sometimes showing wider and narrower portions, as will be seen from the illustrations.

Fixed rules as to the interior shape cannot be given, different fuels requiring a different treatment. The main consideration must be to provide for the increase of volume of certain coals during the period of distillation; for this reason the shaft is enlarged down to the zone of reduction. The walls near this zone should be vertical so as to prevent, as far as possible, the slag from sticking. At the bottom end the shaft is frequently made narrower in order to force the air straight upward, instead of along the side walls. Such a narrowing will never do any harm, as at this point the volume of the fuel is already considerably decreased by the

partial combustion. Vertical walls facilitate the uniform downward travel of fuel.

Poke holes are generally provided in the cover and in the side walls, in order to make it possible for the fireman to reach the interior layers of the fuel and to break up the clinker.

Since in a vertical shaft the fuel is easily kept at uniform height, the shaft producer is used to-day *almost* exclusively, but *always* in cases where the producer plant is not directly connected to the furnace.

Siemens' Producer. The second type, which was developed by Siemens, is used when producer and furnace are built in one unit, Fig. 46. The fuel is charged through a hopper provided at the top and passes over

Fig. 46.

an inclined firebrick wall, which, at the bottom, is continued as a step-grate.

The Siemens type of producer offers less resistance to the passage of the gas through the fuel bed than the shaft type, as in the latter the gas has to travel through the entire height of the coal contained in the producer. For this reason blowers are used in producers of the shaft type, while in Siemens producers in many cases natural draft, produced by a stack behind the furnace, is employed; this, however, frequently necessitates a reduction of the fuel layer and thereby causes incomplete gasification.

The loss produced by the last-mentioned fact is not very considerable, as the gas produced is directly and immediately used and pretty nearly all the heat passing from the producer to the furnace utilized. If, on the other hand, the gas would be cooled before being used, very considerable losses (up to 40 per cent or 50 per cent) would result. Therefore, shortly after the introduction of the Siemens producers addition of steam was

employed by arranging a water pan in the ash pit and producing the steam by the radiating heat.

Half-gas Firing. Within the class of Siemens producers we must also include the so-called "half-gas firings," which are especially used for low-grade fuels. These firings are not supposed to produce complete gasification. The gas produced contains much carbon dioxide. For utilizing the monoxide, an additional supply of air is introduced in the combustion place.

In the charging hopper *B*, Fig. 47, tarry gases and steam are produced by dry distillation. In order to prevent them from escaping during the charging of fuel, connecting channels *D* are provided between the producer *H* and the hopper. These channels are frequently provided with a movable slide. The secondary combustion air enters through tuyeres *A* after being

Fig. 47.

preheated in the brickwork. It is a disadvantage that these producers depend on the chimney draft, because the latter is governed by atmospheric conditions. Hence, even in these producers artificial blast has been resorted to, which permits the use of a higher fuel bed. Fig. 48 shows this new development of the Siemens producer (four producers combined to one unit), which is very similar to the shaft type.

Continuous operation is especially desirable with installations containing only one producer, while in plants comprising a number of producers an alternate disconnection for cleaning purposes is possible. If one main is supplied from several producers, the uniformity of the gas is increased.

The charging appliances of gas producers must be so arranged that the production of gas is not interfered with during the operation of charging. This is effected by bell hoppers.

In all these hoppers the fuel to be charged is first transported to a hopper space, which is separated from the producer space proper by an

air-tight bell. Then the upper door of the hopper space is closed and by opening the bell the charge is allowed to run into the producer. Fig. 49 shows such a hopper. The charging is done at certain intervals, which

FIG. 48.

causes a change in the uniformity of the gas, as the dry distillation of the green coal is not going on uniformly.

Ebelman Method. In order to produce a more uniform gas and to reduce the manual work, continuous charging has been tried by various ways. The first, suggested by Ebelman, Fig. 50, in the first half of the nineteenth century, consists of the application of a charging shaft, from which the fuel gradually travels to the zone of combustion. The gas is drawn off outside the charging shaft, whereby the latter assumes the temperature of the escaping gas. This causes the generation of gas already in the shaft and makes the use of a bell hopper, Fig. 49, unavoidable, except in cases where still larger quantities of fuel are kept in readiness above the charging shaft. The latter is generally made of cast iron, and is gradually destroyed if exposed to high temperatures.

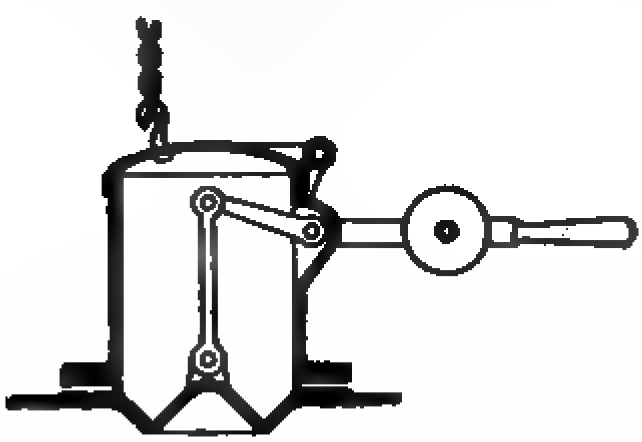


FIG. 49.

Fig. 50.

Fig. 51.

Fig. 52.

Buire-Lencauchez Producer. In the producer of Buire-Lencauchez, Fig. 51, the gases escape through the charging shaft.

Zetzsche has gone still further by so developing this central pipe that it can be lengthened or shortened, whereby the height of the fuel bed can be regulated according to the quality of the fuel. The lower rings of the pipe can be easily exchanged if necessary.

Fig. 53.

A second method of charging continuously employs various mechanical appliances, the first among them having been constructed by Bildt Fig. 52. A water-seal producer with Bildt feed is shown in Fig. 53; while there are a considerable number of other mechanical charging devices on the market.

Removal of Ash. Another important part of the producer is the means for removing the ash and clinker. Here the aim is also to reduce the manual work and to decrease the loss of combustibles through the

ash. In the old Siemens producers up to 10 per cent of the fuel was found in the ash, later producers showed a loss of 5 per cent, while in modern producers the loss is said to be reduced to 1 per cent or $1\frac{1}{2}$ per cent. Further aims are the removal of clinker without discontinuing the operation of the producer and accessibility of its respective parts.

Blowers. We will now say a few words regarding the blast, which is produced in all, or nearly all, plants by means of steam jet blowers,

A

Fig. 55.

Fig. 54.

Fig. 56.

which are the most convenient appliances to that end, as they do not get out of order; furthermore, every producer is, and remains, independent with respect to the blasts if the latter is produced by steam jet blowers. (For very wet fuels, as certain grades of peat and lignite, dry blast has to be used, as is easily understood.) The steam jet blower must be properly constructed in order to produce economically the highest possible steam velocity.

Fig. 54 shows the well-known Koerting blower with spindle. *A* is the air inlet, *R* the regulating spindle, *S* the steam connection, *M* the

nozzles. With ordinary bituminous or hard coals there is no difficulty to so regulate the quantity of air by means of the steam jet blower as to get dry gas. It is hardly necessary to lay stress upon the self-evident fact that the steam used in these blowers should be dry.

Fig. 57.

A high-pressure blast is of no advantage in the operation of producers, as it means an unnecessary loss of energy, formation of holes and deterioration of the gas.

In Fig. 55 is shown the ash pit of a producer without a grate. The ash rests upon a firebrick base, the air enters through the sides as shown by the arrows. In a vertical producer of considerable diameter the air will rise along the wall, the path of least resistance, whereby a dead zone is formed in the center of the shaft, causing a defective production of gas. Therefore in large producers the diameter is frequently decreased toward the bottom.

Fig. 58.

The simple plane grate insures a uniform distribution of the air over the entire area. However, with large diameters the life of the grate is short and the removing of the clinkers a very tedious and difficult operation. Furthermore, the unburned fuel falling through these grate bars represents a considerable loss.

For facilitating the removing of the clinkers in large producers, so-called "false grates" have been resorted to, which at the period of cleansing are inserted above the ashes. In this case the gas production is stopped during cleaning. Turk's producer, which is illustrated in Fig. 56, shows in slit *e* the place where the false grate is inserted above the grate *h*.

Fig. 59.

Step grates are also sometimes employed. Fig. 57 shows such an arrangement in a Turk producer. Fig. 58 illustrates a Poetter producer with so-called polygonal grate. The removal of the clinker from these producers is by no means an easy job. The loss through fuel getting into the ash is 5 to 6 per cent.

Of similar construction is the producer with basket-shaped grate, which is built by Paul Schmidt and Desgras. It is mainly used for lignite briquettes. The channels for the admission of air also support the circular lower grate beam. The ashes rest in most of these constructions upon the bottom of the ash pit, which is covered with water. Sometimes also plane grates are used at the lowest point of the grate

region. The Mond producer shows a similar construction around the grate.

In all these producers the clinker accumulations formed must be loosened through the grate slits. Hence the various parts have to be removable and exchangeable. In order to facilitate the removal of

FIG. 60.

the clinkers, Schneefuss has proposed a shaking grate of basket shape suspended on chains.

During the period of removing the clinkers, the operation must be interrupted in all these producers, as the ash doors have to be opened.

Water Seal Producer. If the operation of the producers is to be continuous, the ashes and clinkers must be removed during the operation. This is effected either by a water-seal or by mechanical draft appliances.

A typical producer with water seal as constructed by Poetter & Company is shown on Fig. 59. The combustion air is introduced through a central pipe. The hot bed of ashes effects a posterior combustion of carbon particles which might have escaped combustion and causes a better distribution of the air.

The Morgan Producer. In the Morgan producer Fig. 60, which gives excellent results—the loss of fuel in the ash being reduced to 1 per cent to 1½ per cent—the air is introduced in the center, while Schlueter Fig. 61 arrives at good results by introducing air at the sides through a certain number of tuyeres and by suitably reducing the diameter of the producer in the zone of combustion.

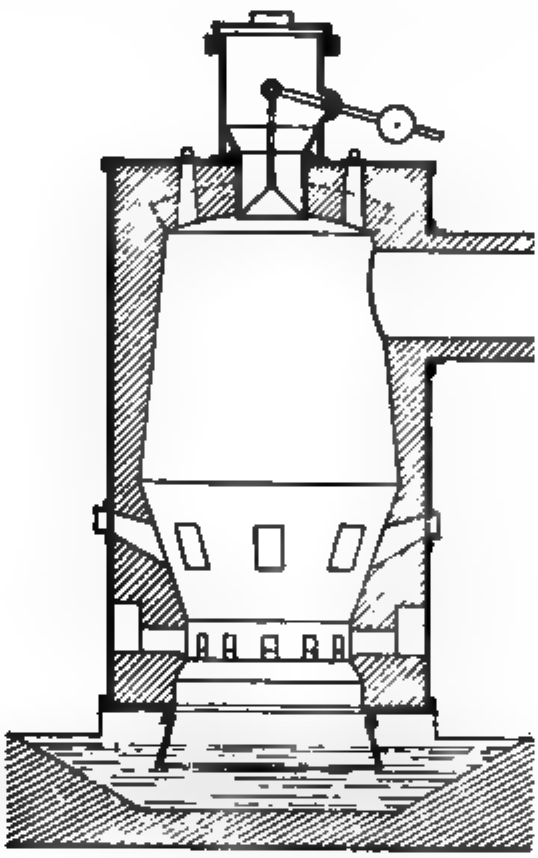


Fig. 61.

Fig. 62.

As part of the water of the seal is evaporated by the heat of the ash, the quantity of water (steam) put into these producers must be reduced. The clinkers are loosened by poke-holes in the walls. A producer of remarkable simplicity in which the removal of ash and clinkers is easily performed is the Duff producer, which in the Bradley modification is shown in Fig. 62.

The special feature of this producer is the use of four blowers and four grates. It is to be stated that, while only two grates are shown in the cut, a dividing plate is provided between each grate. This makes practically four independent grates. For instance, should the fire get too hot at either of the end walls running parallel with the grate, the blowers controlling those halves of the grates are closed down partly or entirely, as the case may require. This applies also to the center halves of the grates, which are controlled and regulated in the same manner.

Hence an excellent control of the condition of the fire is effected by the regulation of the steam and air blast.

For the removal of ashes mechanical arrangements have also been constructed. The Taylor producer Fig. 63 was among the first of this kind. In this type a solid circular bottom plate or table carries a deep bed of ashes and is arranged to revolve; the revolving of this table discharges the ash and clinker over the edge into a sealed ashpit beneath. The table is revolved by means of a rack under the table, engaging with a pinion on a shaft driven by hand or power gearing substantially attached to the outside of the lower casing. Suitable guides hold the table carefully.

Fig 63.

The grinding is done as fast as the ashes rise too far above the desired line—say, every six to twenty-four hours, or according to the rate of working. The bed of ash is kept about 3½ ft. deep on the revolving table in the larger sizes.

Another example of a self-cleaning continuous producer is the Hughes type, shown in Fig. 64. This producer is divided into two parts, the upper and the lower, with a water seal between, the upper portion rotating mechanically. By means of an iron bar, thrust between the ash table and the revolving part of the body, the clinkers are broken up and with the ashes fall into the ash receptacle beneath. By opening an outlet valve at the bottom of this cone-shaped ash receptacle the ashes are discharged into cars underneath.

The upper shell of the producer is made of steel plate riveted to and resting upon a steel ring, forming a combined tread and rack. This rack is driven by a vertical shaft and pinion connected to the main driving shaft by a train of gearing. Thus the upper shell is rotated as above mentioned. The tread of this steel rack travels on conical chilled iron wheels having tight axles revolving in self-oiling boxes.

FIG. 64.

A further development as far as the rotation of the grate parts is concerned is the Kerpely producer, shown in Fig. 65. The rotating plate is developed as water seal and carries the grate, which consists of several plates, through which the air passes into the producer. The lower part of the grate disintegrates the clinkers and the latter are automatically

removed from the water seal by means of a shovel. One rotation is made in three hours.

In the Rehmann producer the rotating parts consist of suitably arranged cones, which are provided with perforations through which the air enters. The arrangement of the shovels for removing the ash is shown in Fig. 66. The larger pieces of clinkers are raked out, the smaller ones shoveled out.

In these producers the ash is loosened and the clinker disintegrated. We will now discuss the next step—the mechanically poked producers.

The Fraser-Talbot producer Fig. 67 pokes the fuel by means of two agitators arranged on a vertical shaft.

The latest development along these lines is the Hughes producer Fig. 68, in which the mechanical poker is a water-cooled steel casting suspended from a trunnion. The poker is operated by ratchet gearing actuated by a crank and crank-shaft which is driven by a reduction gearing connected to the main shaft. This mechanism moves the poker back and forth, agitating and breaking up the mass of fuel, and evenly distributes the coal and helps in working down the ashes for removal. The uniform treatment secured by the mechanical poker gives better and more uniform results as to quality, quantity and supply of gas, and reduces the cost of installation and operation. The power required to operate a single producer is 3 electric horse-power. Twenty-five pounds of coal are gasified per square foot.

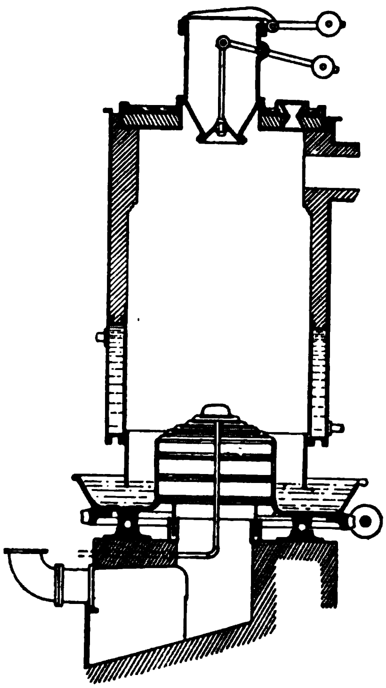


FIG. 65.

The Combustion of Producer Gas. High efficiency of combustion depends on thoroughness of the gas-air mixture, and on preheating the air. In order to obtain a temperature of bright red incandescence it is imperative to preheat the air for combustion by exposing it to the temperature of the hot products of combustion passing to the stack.

A good many devices for mixing the gas and air consist simply of two concentric pipes, one for air and one for gas. In Fig. 69 we have a gas pipe *a*, an air pipe *b*, a collar, *c*; *d* is the opening of the gas pipe, *e* the flue, *f* the hearth, *g* the front plate of the furnace, g^1 the back plate, *i* the connection to the gas line, *k* the connection to the air line. *b* can

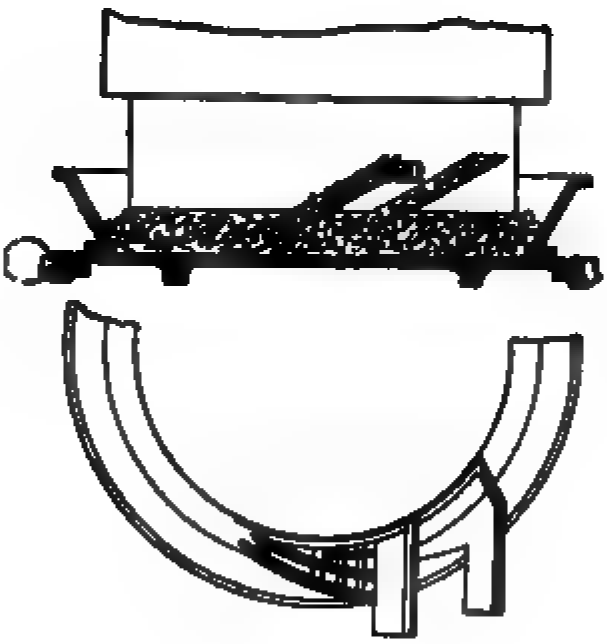


FIG. 66.

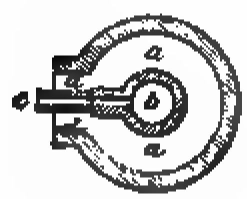
FIG. 67.

FIG. 68

be turned around its axis between the flanges *m* and *n* in order to give the flame the desired angle toward the hearth.

For a downward direction of the flame, the burner shown in Fig. 70 is very practicable; *b* is the air, *a* is the gas pipe.

The manner in which gas and air meet is of great importance for proper combustion. By a suitable arrangement of the gas and air channels a long or short flame can be produced. If air and gas are brought together at right angles Fig. 71 a rapid, concentrated combustion is effected. For every gas channel there is a corresponding air channel.



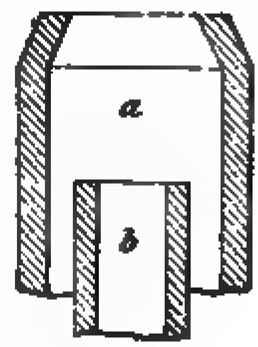


FIG. 70.

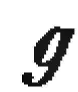


FIG. 69.

FIG. 71.

The arrangement shown in Fig. 72 effects a more rapid combustion as the gas rises toward the horizontal air current. The air, on account of its higher specific gravity, rapidly mixes with the gas.

If the currents of gas and air are carried parallel into the furnace, the combination of gas and air is gradual and a long flame is the result. Fig. 73. The flame is shortened if gas and air enter at an angle Fig. 74.

Another method is shown in Fig. 75. The air enters through slit *l* and the gas is blown through, drawing along a sufficient amount of air from *l*. Gas and air meet in *m* and are burned in *v*.

The small furnaces used in the metal industries for tempering and annealing are still generally heated by illuminating gas or other rich gases. However, they can also be used for producer gas, if the gas and air have a sufficiently high pressure. The temperature obtained increases with the pressure.

In order to obtain the highest economy in gas-fired furnaces where high temperatures are to be reached, successful use may be made of the principle of regeneration, i.e., of storing the waste heat in regenerators (heat storers consisting of chambers filled with firebrick checker work). It is evident that the gas and air currents must travel in a direction opposite to that of the products of combustion, if it is desired to transfer

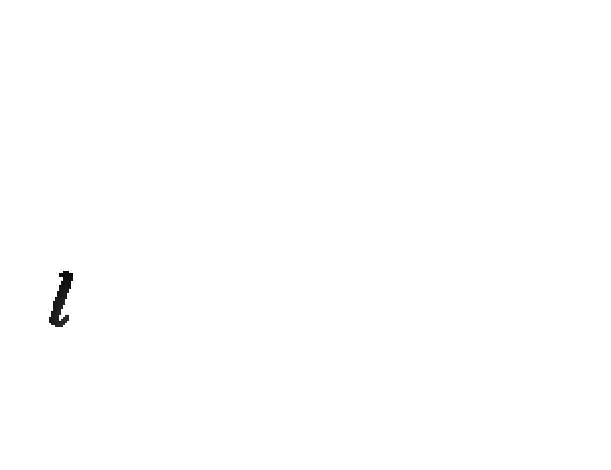


Fig. 72.

Fig. 73.

the sensible heat of the waste gases to the incoming gas and air. It follows that a regenerative furnace consists of two symmetrical parts, the axis of each going through the reversing mechanism. Each part consists of an air regenerator and a gas regenerator or of an air regenerator only.

The two air regenerators are connected by means of a reversing valve. Also the two gas regenerators.

Fig. 76 shows the plan of a regenerator system. *hh* are the air, *h'h'* the gas regenerators, *a* the air, *a'* the gas-reversing valve, *c* the gas main,

Fig. 74.

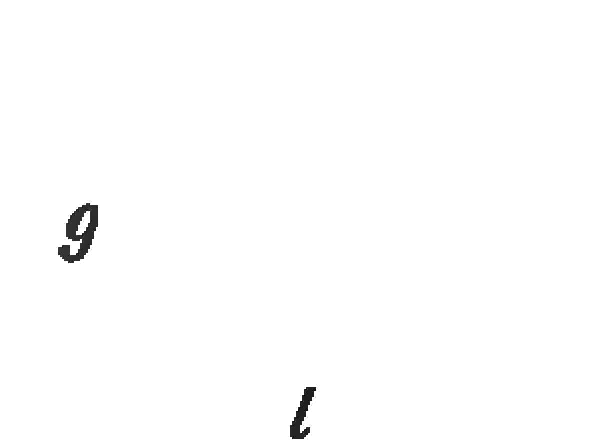


Fig. 75.

b the opening for the air for combustion, *a* the stack. At the position of the valves shown air and gas travel to the left, combine in the flue above *e*, pass as flame over the hearth through the right-side regenerators and valves and leave through *d*.

For comparison of direct firing with gas firing we show in Fig. 77 a directly fired furnace and in Fig. 78 the same type of furnace after its transformation to gas firing. First of all, we note the more convenient

Fig. 76.

Fig. 77.

Fig. 78.

way of charging the fuel to the gas-fired furnace, the fuel being charged through a door *t* on top, while with direct firing the fuel has to be thrown in through the front door. The grate *r* carries in the first case a low bed of fuel and complete combustion to carbon dioxide takes place. In the second construction (gas fire) the grate carries a high bed of fuel and the effective gas is carbon monoxide.

In the first type of furnace the products of complete combustion heat the hearth and escape through the stack, in the second type the complete combustion takes place at the hearth, just where it is wanted, and the heat stored in the firebrick work below the hearth is utilized for preheating the air for combustion, passing through a flue *l* provided for this purpose. This comparison shows the greater convenience and higher economy of gas firing.

Gasification. The generation of producer gas is based upon "gasification," i.e., the transformation of the free carbon of the fuel into carbon monoxide, and it is easily understood that for this process a fuel containing the largest amount of carbon and the smallest amount of volatile matters will be most desirable. Such fuels as anthracite, charcoal and coke, however, though easily transformed into a gas free of tar, are too expensive to be used in the big industries, which are forced to use bituminous coal, wood and lignite.

In small producer plants, especially in connection with gas-power plants, the higher price of anthracite is outweighed by its greater convenience. But even here conditions are changing and the use of bituminous fuels is being slowly but surely introduced.

The gasification of the carbon in the producer is effected in such a manner that the carbon is first burned to carbon dioxide, the latter being then reduced to carbon monoxide by contact with additional carbon. Hence, carbon monoxide is the essential component of producer gas. The perfect reduction of dioxide to monoxide takes place, theoretically, at a minimum temperature of 1000° C., which is easily produced by combustion to carbon dioxide. At lower temperatures part of the dioxide is not reduced, the formation of the monoxide stopping entirely at about 450° C.

Height of Fuel Bed. The height of the fuel bed in producers necessary for complete reduction varies with the quality of the fuels used. Dusty fuels require less height than coarse, loose, fuels. The proper height for 1-in. coke is 30 in.; for $1\frac{1}{2}$-in. coke, 45 in.; for $2\frac{1}{4}$-in. coke, 72 in.; for $\frac{3}{4}$-in. bituminous coal, 22 in. are sufficient; for run of mine, 60 in. to 80 in.

With bituminous fuels too high a fuel layer is not to be used, as this causes an increased formation of tar and soot, for the volatile matters and the moisture escape from the higher zones before the fuel reaches the incandescent zone of reduction. The higher the temperature of the upper layers, the thinner will be the tar produced and the more hydrogen and

methane will be found in the gas. The two latter components increase the thermal efficiency, but the tar, together with the soot, are disagreeable impurities of the gas, more so if the gas is cooled before its use.

As stated above, a temperature of not less then 1000° C. is required for complete formation of carbon monoxide. If considerably higher temperatures are applied, the disadvantages will be found to outweigh the advantages, as by such high temperatures the firebrick lining is rapidly destroyed and the ashes of the fuel always obtained as molten slag.

Such slag formations occur with various grades of fuels, depending upon the composition of the ash, at higher or lower temperatures. In the latter case it can only be avoided at the expense of the gas production. Here the addition of water to the gasifying air is a simple remedy, which, at the same time, increases the thermal value of the gas and the efficiency of the producer, simultaneously cooling the grates of the producer.

Water in Gasification. Incandescent coal decomposes water into its elements. The hydrogen formed enriches the gas and the oxygen combines with the carbon to carbon dioxide or monoxide, according to the prevailing temperature. The formation of monoxide by the decomposition of water is most complete at a temperature of 1000° C., while at lower temperatures more and more carbon dioxide is produced. In practice, however, it is impossible to decompose all the water contained in the gasifying air. One part goes always unchanged through the producer and increases the moisture content of the gas. If this moisture is present in the gas during its combustion it has a heat-consuming effect and decreases the temperature of combustion.

Hence, no water is to be added for the gasification of fuels rich in water, and some fuels require even drying, if with the gas produced a somewhat high temperature is to be reached. It is also evident that the temperature of the gas leaving the producer decreases with the temperature of the producer and with the increasing amount of heat which is disposible for degasification and evaporation.

If, for instance, in the gasification of dry bituminous coal the temperature of the gas leaving the producer is 600° to 800° C., a temperature of only 400° to 500° C. will be observed if water is added.

Of great importance is the question: How much water may be advantageously added? Fuels with a large percentage of volatile matters can stand only a small addition of water, as, during their degasification, much water is formed. If such fuel is also very moist, the result may be a non-combustible gas.

The amount of water added must be regulated so that the walls of the producer do not suffer by the heat and that, as much as possible, the formation of liquid slag is avoided.

In gasifying pure carbon 1 kg. of water may be added to 4.5 cu. meters of cold gasifying air without causing any loss of heat and as for

gasifying 1 kg. of carbon about 4.5 cu. meters of air are required, the upper limit of the addition of water is about 1 kg. to 1 kg. of carbon.

If the air of combustion and the water added are preheated the quantity of the latter may be increased and may reach at 550° C. double the amount mentioned above. This explains why in practical gasification of coke, which is practically pure carbon, 300 to 400 grams of water are added per cubic meter of air if a gas rich in hydrogen is to be produced.

In gasifying bituminous coal for the production of a gas not too rich in hydrogen, 150 to 200 grams of water are taken per cubic meter of air. From a theoretical point of view, however, a somewhat larger addition of water is nearly harmless, so far as the utilization of the fuel is concerned. It is true that in such a case a larger quantity of carbon dioxide will remain unreduced, but with the increased quantity of decomposed water, also more pure oxygen will get into the producer. Hence, less gasifying air is required, which means a decrease of the nitrogen content of the gas produced.

The composition of producer gas varies a great deal. Under normal conditions, if a good grade of fuel is used and the operation properly carried out, the gas will contain about 25 per cent of carbon monoxide. If the producer gets very hot, caused by the total or nearly total absence of water, the content of carbon monoxide may be up to 30–31 per cent.

The second combustible component of producer gas is hydrogen, varying in quantity between 8 to 14 per cent. However, the hydrogen content may be even higher or lower, depending upon the moisture of the gasifying air and other conditions. Some factory managers are afraid of too high a content of hydrogen and believe that it does harm to the firebrick and affects the finished product disadvantageously.

So far, however, continued operations with producer gas from peat, which is rich in hydrogen, have been and are being carried out successfully; the harm—if any—done must be due to some other cause, probably to the moisture of the gas, which causes decomposition of and recomposition to water, thereby effecting numerous disagreeable complications. Accordingly a gas rich in hydrogen would have to behave differently, when cooled (dried) before its use or when used hot.

That the hydrogen cannot be the only cause of the above-mentioned complications (sudden rise of temperature) is shown by the fact that carbon monoxide in combustion, though not yielding as many thermal units as hydrogen, produces a higher temperature. Hence, a gas, which on account of its high content on hydrogen, has a higher thermal value as compared with others, may be equivalent to the latter, as far as the temperature of combustion is concerned.

There is a certain relation between the percentage of carbon dioxide and the percentage of carbon monoxide and hydrogen. That it is not

always of advantage to get a gas with the lowest possible content of carbon dioxide we can see from the fact that at dry gasification, where very little dioxide is formed, the efficiency of the producer is much lower, as with a large addition of water.

On the other hand, the content on dioxide is also influenced by the nature of the fuel, as with low melting slag the temperature must be kept so low that the complete transformation of dioxide into monoxide is prevented. Some grades of coal, therefore, will only difficultly be gasified at reasonable economy if the formation of slag is not taken into consideration and if the producers are not constructed to suit these conditions. As a rule the carbon dioxide should not go above 3 or 4 per cent.

The methane gets into the producer gas from the products of decomposition of the volatile matters. The quantity of methane varies from 1 to 3 per cent and depends upon the temperature of degasification. The heavier hydrocarbons are also sometimes found in traces if the temperature of degasification is very high.

If the tarry compounds of the gas are decomposed in the producer, the composition of the gas is changed, the percentage of carbon dioxide and hydrogen is decreased, of the monoxide increased. As the hydrocarbons have a high thermal value their presence is desirable, especially if high temperatures are to be reached.

Some oxygen is also generally present in producer gas. Leaks and holes in the fire are mostly the causes of its presence. The rest of the gas is nitrogen, which, at dry gasification amounts to 60 per cent, at moist gasification to about 50 per cent.

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VI

POWER AND POWER TRANSMISSION

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Sources of Power. Fuel and water power are the two general sources of power. The heat from the fuel produces steam from water in a steam boiler, and from the expansion of this steam through the use of a steam engine or "steam turbine" mechanical power is obtained. In the utilization of the power of a water-fall the transfer of energy is more direct, the force of the water against the buckets on the rim of a wheel furnishing the driving force for the shaft of this wheel. The principles involved in the production of power from these two sources will be outlined and discussed.

Steam Boilers. Steam boilers may be divided into two general classes: fire-tube boilers, in which the hot gases from the fire pass through a series of tubes surrounded by water, and water-tube boilers, in which the water is in tubes and the hot gases circulate around the tubes. The latter cost more, but are less liable to explode, and the steam pressure can be obtained in a shorter time. Small vertical boilers are used, chiefly for portable work; but their efficiency is low, and the steam pressure variable under heavy load. The larger sizes of vertical boilers are used where floor space is limited and where there is plenty of overhead room.

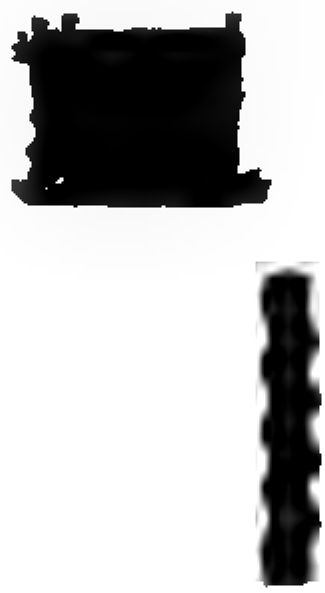


Fig. 79.

Horizontal Water-tube Boilers. A general view of a horizontal water-tube boiler is shown in Fig. 79. A general idea of the cost of steam boilers is given in Fig. 80. The average efficiency of steam boilers is about 60 per cent, and under the best conditions of actual practice it may rise as high as 75 per cent: that is, about 40 per cent of the heat units produced by the combustion of the fuel go up the smokestack in heating the waste gases. A small proportion of the loss is due to radiation of heat from the boiler. With crude oil for fuel, the efficiency

of some steam boilers is increased about 5 per cent. With low grades of coal mechanical draft may be used to advantage, whereby a fan driven by a small engine or motor forces the air through the fire. This takes

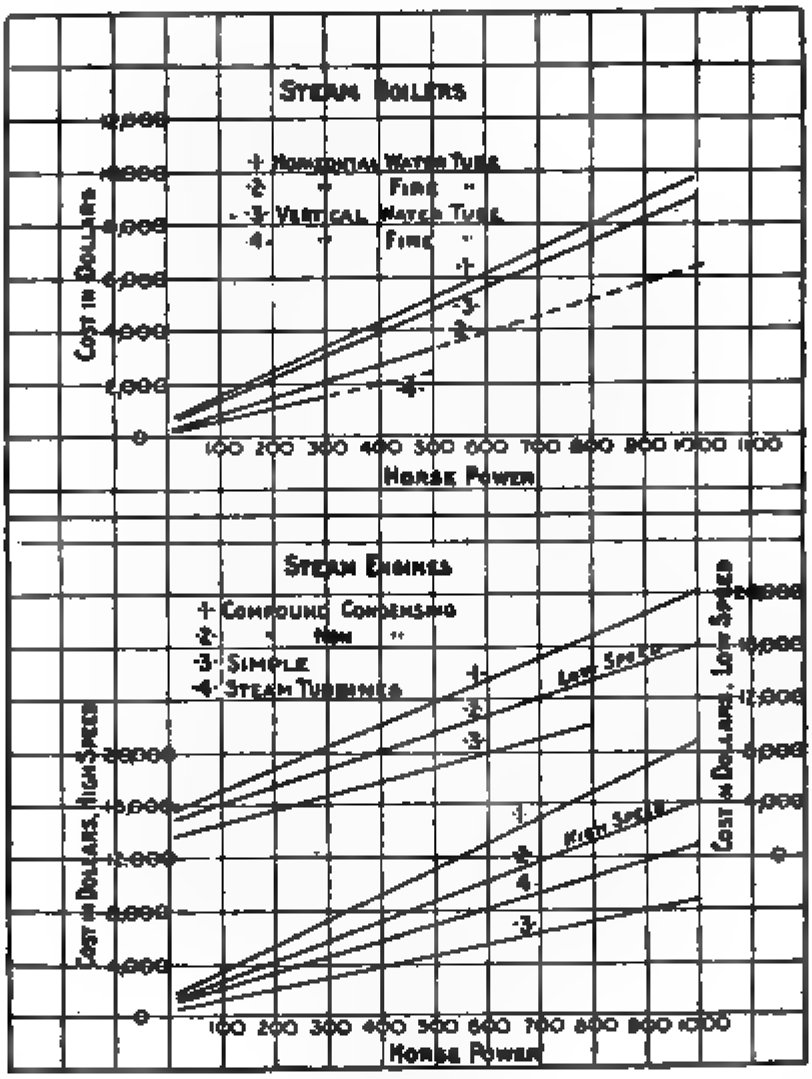


Fig. 80.

the place of a very tall chimney, and gives more complete combustion. Mechanical draft, where the cost for the foundation is great, frequently is used in place of an expensive chimney.

Steam Engines. Steam is taken from the boiler through iron pipes to the cylinder of the steam engine, shown in Fig. 81. The steam expanding here forces the piston back and forth, the input of the steam being controlled by an automatically operated valve. The piston rod, being attached to the main shaft of the engine, produces a continuous rotation of the shaft.

Fig. 81.

Steam Turbines. Another method of applying steam has been developed in the steam turbine. In this, steam, flowing at a high velocity, strikes a large number of vanes or blades, thus driving the

shaft at a radius depending upon the diameter of the turbine wheel. A steam turbine necessarily runs at a high speed, on account of the high velocity of the steam. On account of the higher speed of steam turbines, they take less space as a rule than the ordinary reciprocating steam engines. The high speed, however, makes them unadapted in some instances for running slow-speed machinery, except through electrical transmission of the power. Referring to Fig. 82, it will be noticed that the efficiencies of steam turbines and of good reciprocating engines are about the same. There are many special cases where steam

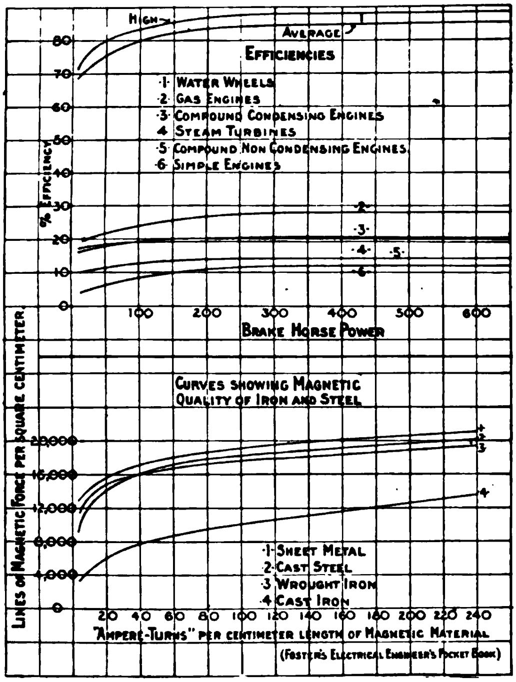


Fig. 82.

turbines can be used to great advantage in manufacturing plants; such as using live steam from a high-pressure boiler for cooking certain raw materials, when in place of a "reducing valve" a low-pressure turbine may be employed, thus making a saving in mechanical power.

Cost of Engines and Turbines. The general cost of different types of steam engines, and of steam turbines is given on Fig. 80. It will be noticed that slow-speed machinery costs more than high-speed machinery. For a given output the higher speed has less size and weight. The difference between "simple engines," "compound non-condensing," and "compound condensing" engines consists in more expensive auxiliaries, which increase the first cost for the compound condensing engines. A higher efficiency, however, is obtained for the

compound condensing engines, due to the low consumption of coal per horse-power. In figuring the cost of a power plant, using either steam engines or steam turbines, the cost of the auxiliary apparatus, such as piping, feed-water heaters, etc., must be taken into account. These auxiliaries vary so widely in different power plants that accurate figures cannot be given. The cost curves in this chapter are for general comparisons only, and to give an idea of the relative costs involved. The efficiency of a steam engine or steam turbine varies with the load applied, as can be seen from Fig. 83. It is good practice to keep each unit or engine in the power station as near full load as possible throughout the day, rather than to have all of the engines of the station running under partial load.

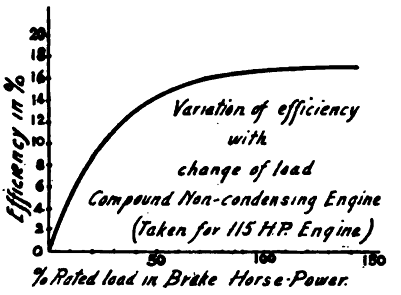


FIG. 83.

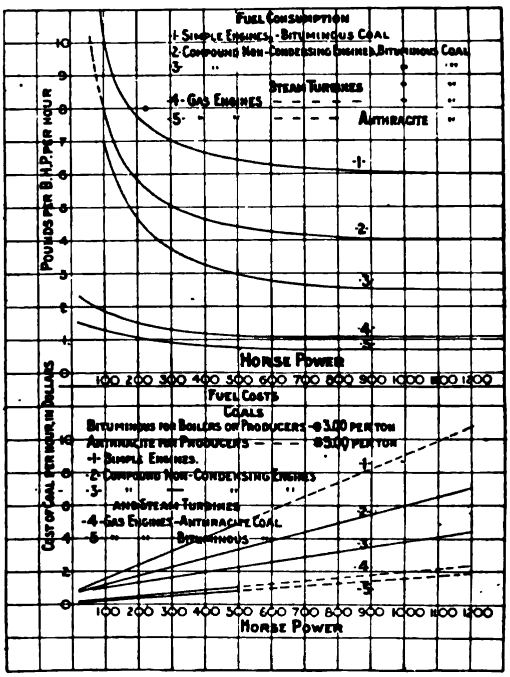


FIG. 84.

The boiler horse-power may not be the same as the engine horse-power of the plant. The horse-power used in plotting the curves in these figures means brake horse-power (B.H.P.), that is, the actual power obtained from the shaft of the steam engine; whereas the boiler horse-

power is a rating depending upon the ability of the boiler to produce steam. One boiler horse-power means the evaporation of 34.5 lbs. of water per hour at atmospheric pressure. The amount of steam required per brake horse-power per hour varies with the type of engine, the cheaper engines requiring more steam. A small simple non-condensing engine requires about 50 lbs. of steam per brake horse-power per hour, and the very best compound condensing engine, running under the most favorable conditions, takes about 10 lbs. of steam. The relative amount of steam required for each type of engine can be determined from the curves on Fig. 84, which show efficiency and fuel consumption. In general, the boiler horse-power required for the average steam pressures used can be determined by dividing the total horse-power of the engine, multiplied by the steam consumption for that particular type, by 34.5, and adding from 5 to 10 per cent to the result obtained. For example, a large city lighting plant using compound condensing engines might take 17 lbs. of steam per brake horse-power per hour, and the boiler horse-power required in that case would be about one-half, plus 10 per cent, boiler horse-power for each engine horse-power. A boiler is supposed to develop at least one-third more power than its rating. In comparing two different makes of boilers, the efficiency of the boilers should be taken into account, as the lower priced boiler may have such a low efficiency as to more than offset any difference in cost.

Fig. 85.

Gas Producer Plants. Within the past few years a new type of power plant has been developed, called the "gas-producer" plant. The coal, in place of being burned directly, as in the case of the steam boiler, is heated so that the combustible gases are driven off. These gases are conveyed to "gas engines,"[1] where the gas is exploded in the cylinder; the action being the same as the gasoline explosion in the cylinder of a gasoline engine. This method of getting the energy from the coal secures a higher efficiency, one horse-power per hour being obtained by the combustion of $1\frac{1}{2}$ lbs. of coal; whereas for a steam plant of the same capacity, from 2 to 4 lbs. of coal per brake horse-power per hour are required. In Germany, where the

[1] Sheffield Gas Power Co.

cost of fuel is such an important item to the manufacturer, gas-producer plants of all sizes have been developed to a very high degree of efficiency. In this country there is an increasing development of this type; so that the future production of power from coal may be largely through the use of the gas-producer plant.

A general idea of the construction of a gas-producer is given in Chap. V and of a gas engine in Figs. 85 and 86. The cost of gas producers depends somewhat upon the type and nature of the fuel to be used, varying from about $14.50 per horse-power for use with good anthracite coal about $23 for lignite and bituminous coal. Special equipment for taking care of the by-products accounts for the extra cost for the lower grades of fuel. The cost connected with gas-producer plants can be determined in general from the curves in Fig. 87; the relative efficiencies and fuel consumptions are given in Figs. 82 and 84.

Fig. 86.

Small Special Power Plants. Gasoline engines have been developed that give very satisfactory service for small isolated plants, supplying power for lights and for driving machinery requiring a few horse-power. Denatured and wood alcohol are also coming into use as fuel, and will probably find more extensive application in the future.

Water Turbines. The power of water-falls is made use of by means of water-wheels or water-turbines. The old form of water-wheel consisted of a large wheel, usually made of wood, with buckets on the outside rim; the water flowing into these buckets forced the wheel around by its weight. In another form the water was made to flow over the top of the wheel, the power being derived from the force of the water combined with its weight. This is known as the "overshot" wheel. A third form, the "undershot" wheel, has water carried to the bottom of the wheel through a narrow outlet, the impulse of the moving water forcing the wheel around. Modern water-turbines have been developed, using also the principle of "reaction." The water, flowing into a bucket and rushing out again, produces a force in a direction opposite to the water moving away from the wheel. A

cubic foot of water weighs 62.5 lbs., and this weight acting through 1 ft. corresponds to 62.5 ft.-lbs.; 33,000 ft.-lbs. per minute is equal to one horse-power. Consequently the theoretical horse-power of a water-fall is determined by the effective height of the fall and by the number of cubic feet of water per minute flowing over the fall. The actual power delivered at the shaft of a water-turbine depends upon the size and type of the turbine. The general efficiency curves are given in Fig. 83. It will be seen that from 15 to 35 per cent of the power of a water-fall is wasted through inefficiency of water-turbines.

Turbines in general may be divided into two classes: "low head" for use up to about 200 ft. of fall, and "high head" for higher fall. Less than 30 ft. may be called a very low head. High-head turbines have been employed in mountainous districts in falls of over 2000 ft. The number of cubic feet of flow of water per minute in such cases is comparatively small. The cost of water-turbines and auxiliary equipment varies so widely, with particular conditions, that nothing but the general figures of Fig. 87 can be given. Low-head turbines produce slow speed, and hence demand heavier machinery with consequent greater cost. The speed of a water-turbine is controlled by a piece of apparatus called a "water-wheel governor," that automatically operates the gates or valves that control the amount of water admitted to the turbine. This device keeps the speed very nearly constant, about 2 per cent variation, from no load to full load.

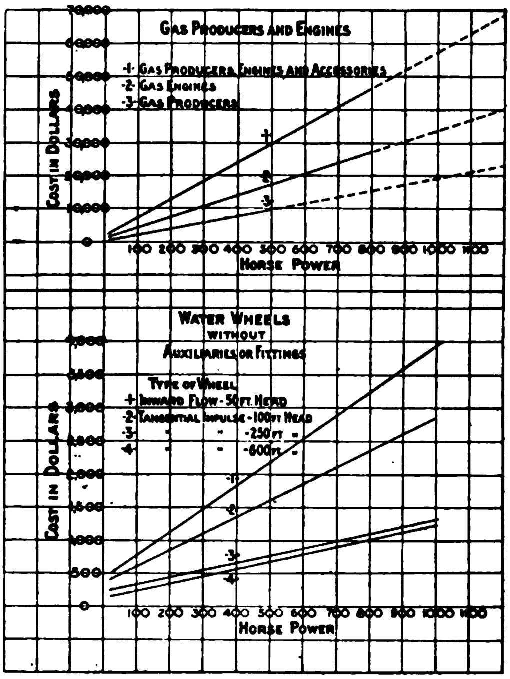


Fig. 87.

Transmission of Power. In some plants the power of the water-turbine shaft is utilized directly at the water-fall, such as with the grinders used in certain pulp-mills; but in most cases the power is used at a distance from the water-fall, and must be transmitted to a town or city where the manufacturing plants are located. For very short distances the power can be transmitted by means of belts and shafting, but for the longer distances the power must be transmitted electrically. With a reasonably high head

of water compressed-air systems may be used economically for a transmission of several hundred feet. A simple form of compressed-air plant operates on the principle of the Bunsen filter pump, the running water taking in air and conveying it to a chamber under pressure.

Electric Transmission. In order to transmit power electrically the steam engine, gas engine, or water-turbine furnishes the power to drive the electric generators that convert mechanical energy into electrical energy. An electric generator or "dynamo" develops an electrical pressure, and this pressure causes an "electric current" to flow in an electrical conductor in much the same way that a pump produces a pressure in a water-works system. In an electric circuit the pressure is measured in "volts" by an instrument called a "voltmeter." The current flowing in the wire is measured in "amperes" by an instrument called an "ammeter." The electrical resistance in the wire corresponding to the friction in the water-pipe, is measured in "ohms." The smaller the pipe the more the friction to the flowing water, and the smaller the electrical conductor the greater the electrical resistance. The electrical resistance decreases directly as the area of the cross-section increases, and increases directly with the length of the conductor. Glass, rubber and air are such poor conductors that they are called "insulators."

Calculations for an Electric Circuit. A simple law gives the relation between electrical pressure, current, and resistance. The current (in amperes) $= \frac{\text{pressure (in volts)}}{\text{resistance (in ohms)}}$. For example: a 16 candle-power, 110-volt incandescent carbon lamp has 220 ohms resistance, the current flowing through the carbon filament is then $\frac{110}{220} = \frac{1}{2}$ ampere. The light does not consume this current any more than a water-power station consumes the water of the river, for the reason that as much water flows away from the station as flows to it. In the case of the incandescent lamp this one-half ampere flowing through the carbon resistance or filament, at the very high velocity of light, produces enough molecular friction to bring the filament to a white heat. From the above formula it will be noticed that the higher the resistance of the circuit the less the current that flows. The power of a water-fall is proportional to the height of the fall times the amount of water flowing over the fall. With twice the volume of water the power of the fall is doubled. The same is true if the height of the fall could be doubled. A similar general principle appears in an electric circuit—the pressure in volts times the current in amperes gives the power directly in "watts"; 746 watts equals one horse-power, and 1000 watts equals 1 "kilowatt." In the case of the incandescent lamp referred to above, volts times amperes $= 110 \times \frac{1}{2} = 55$ watts. Each light taking 55 watts means that one horse-power will supply $\frac{746}{55} = 13$ incandescent carbon lights of 16 candle-power. A kilowatt would therefore furnish power for

about 18 lights. Where electrical energy costs 16 cents a "kilowatt-hour," it means a cost of about one cent an hour for each 16 candle-power light. A 32 candle-power carbon light requires 110 watts, and an 8 candle-power light about 28 watts. The tungsten incandescent lamps take about one-third the number of watts for the same candle-power as the carbon lights, but cost about three times as much. The saving per month in the electric light bill more than offsets the greater first cost of the lamps. The tungsten lamp furnishes a better quality of light than the carbon lamp.

Static Electricity. The difference between what is called "static electricity" and the electricity used for electric lighting and power purposes is that the former has a very high pressure with very little current. Static electricity may be compared to a water-fall several thousand feet high with a column of falling water the size of a silk thread. The electricity from batteries or from electric generators with low pressure and comparatively large current corresponds to a water-fall short in height and with large volume of water.

Magnetism. The electric current, forced through coils of conducting material, produces magnetism, and this property of the current is utilized practically in all forms of electrical apparatus and machinery. Some materials are "magnetic" and others are not, iron and nickel being examples of the former, while copper, brass, air and wood belong to the lattet class. The magnetic force developed depends directly upon the producr of the number of turns of wire in the coil (shown in Fig. 89) and the current flowing in the coil, this product being technically known as the "ampere-turns." The quantity of magnetism produced by the current passing through the coil of wire decreases directly with the increase of the mean length of the magnetic path. The mean length of the magnetic path is indicated in Fig. 89. Curves are given in Fig. 83 showing the relative magnetic qualities of iron and steel, and indicating the number of ampere-turns required in the coil for a given length of magnetic circuit of iron or steel, in order to produce a given magnetic density. These magnetic densities for electrical machinery vary from 5000 to 8000 lines of magnetic force in cast iron per square centimeter, and from 8000 to 16,000 per square centimeter for magnetic cast steel. Magnetism may be considered as consisting of lines of force extending from the north to the south pole of the magnet, the intensity of the magnetism being measured in so many lines of force per unit area. The ampere-turns required to drive the magnetism of a given density through the air-gap in a magnetic circuit can be found by dividing the magnetic density in the air-gap by 1.257, and multiplying the result by the total length of the air-gap measured in centimeters. The total number of ampere-turns required for a given magnetic circuit, consisting of an iron or steel frame, with part of the path of the magnetism through air, is the sum of the ampere-turns for the iron portion of the circuit plus those required for the air portion of the circuit. These ampere-turns may consist of a large number of turns of wire with a small

current passing through the wire, or a small number of turns and a correspondingly large current.

The Electric Generator. Electrical power obtained from batteries, with chemical action as the source of energy, is too costly where a large amount of power is required. When the power required is small, such as for electric bells and telegraph circuits, this method of production is very satisfactory. Where power is required on a large scale the cheaper method of securing electrical energy through magnetism is utilized. Referring to Fig. 88, if the copper conductor is passed through the magnetic lines of force between the north and south poles of the magnet shown, in the direction indicated by the arrow, an electrical pressure will be produced lengthwise in the conductor. It takes no mechanical pressure to move the conductor through the magnetic lines of force. This electrical pressure produces no current in the conductor unless the two ends of the conductor are connected in continuous circuit, and there is no power involved unless a cur-

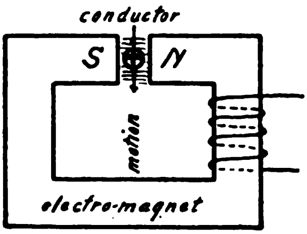


FIG. 88.

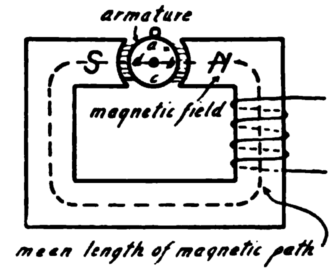


FIG. 89.

rent flows. If to the two ends of this conductor moving in the magnetic field a circuit is connected, the current will flow in the direction away from the observer, as indicated by the + in the end of the conductor representing the tail of an arrow going in the direction of the current. If the conductor is moved in a direction through the magnetic field opposite to the direction indicated by the arrow of the figure, the electrical pressure produced will drive the current in the opposite direction. This action of the conductor moving in a magnetic field may be called a mechanical method for producing an electrical pressure. It is the simplest form of an electric generator or "dynamo."

The Alternating-current Generator. If, instead of moving the conductor back and forth in a magnetic field, a rotary motion is obtained from a revolving shaft, the conductor can be placed on a drum, or "armature," as indicated in Fig. 89. The maximum electrical pressure is generated when the magnetic lines of force are cut at right angles, positions (*b*) and (*d*), and no pressure or voltage is developed when the conductor is moving parallel to the lines of magnetic force in positions (*a*) and (*c*). The electrical pressure produced by one revolution of the drum carrying the conductor is shown by the curve in Fig. 90. This is called an "alternating pressure," and the current resulting from this pressure is alternating. On the opposite sides

of the armature the pressure reverses its direction, because the conductor passes in the opposite direction through the magnetic lines of force. The complete curve from (*a*) to (*a*) is called a "cycle," and the number of cycles per second is known as the "frequency" of the circuit: for instance, a 60-cycle alternating current has 60 positive and 60 negative loops in one second. This is the standard frequency used for alternating-current lighting purposes. The carbon filament of the incandescent lamp tends to cool off when the alternating current falls to zero, but the change is so rapid with 60 cycles that the filament has not time to cool off, and no flickering is noticed in the light. With less than 30 cycles some variation in the light may be noticed, and for this reason low frequency for lighting purposes is to be avoided. If an alternating-current generator has four magnetic poles in place of two, there will be two cycles for each revolution of the armature. When the magnetic poles are revolved and the conductors made stationary, the electrical pressure is developed by the lines of magnetic force cutting the conductors, such a generator being known as the

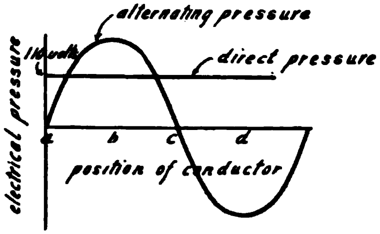


FIG. 90.

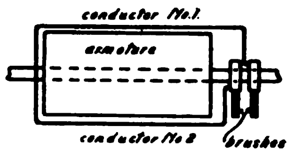


FIG. 91.

"revolving field" type. An alternating-current generator requires unvarying magnetism in the pole pieces, and a comparatively small direct-current generator, called an "exciter," furnishes the current to produce this magnetism.

If two conductors are placed on the armature in a loop, as shown in Fig. 91, the conductors are said to be "in series," and the pressure of one conductor adds to that of the other. The electrical pressure developed depends directly upon the number of conductors in series, the total number of magnetic lines of force cut, and upon the speed of the conductors. Increase any one of these three items and the voltage increases in proportion. For a given speed, and with equal magnetic conditions, a 550 volt generator has five times as many conductors on the armature as a 110 volt generator. A low-speed machine will have more conductors than a high-speed machine of the same voltage. To keep the electrical pressure as uniform as possible the speed of an electric generator, by means of the governor of the steam engine, is kept constant, independent of the load. In order to conduct the electrical pressure from the revolving conductors to the two stationary wires "slip rings," or "collector rings," are used, as shown in Fig. 91. The two ends of the coil of wire on the drum are connected to

two copper rings fastened to the shaft, but insulated from it, and carbon brushes touching these revolving rings carry current to the outside circuit. A circuit having two wires running from the source of alternating pressure is known as a "single-phase" alternating-current circuit.

The Direct Current Generator. To get an electrical pressure that is constant, from which a continuous and unvarying current can be obtained rather than an alternating current, a device called a "commutator" or "rectifier" takes the place of the slip rings, allowing the current to flow from the generator in one direction only as indicated by the straight line of electrical pressure in Fig. 90. The simplest form of commutator is shown in Fig. 92. This consists of two arcs of metal, with mica between them, upon which the stationary brushes rest. It can be seen that as the commutator revolves the upper brush always touches the commutator segment connected to the conductor in front of the *N* pole, so that the current flowing in the upper brush will always pass in one direction. This throws the lower or negative wave of the alternating curve Fig. 90 on the upper side of the horizontal line, and the pressure, although changing in intensity or "pulsating," does not reverse its direction; as shown in the curves

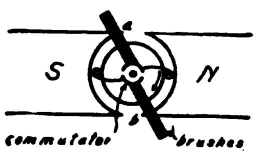


FIG. 92.

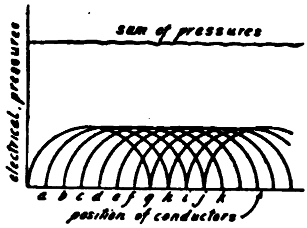


FIG. 93

a, *b*, *c*, *d*, etc., Fig. 93. With a large number of conductors or coils of wire on the armature, and with a corresponding increase in the number of commutator segments, there is developed a large number of individual voltages, *a*, *b*, *c*, *d*, etc., each producing a maximum electrical pressure at a different instant, as indicated in Fig. 93. These turns of wire are so placed on the armature and connected to the commutator segments that they add their voltages: and the sum of all these individual pulsating pressures give practically an unvarying voltage between the brushes. The sparks sometimes seen at the surface of contact between the stationary brushes and the moving commutator have nothing whatever to do with the generation of the electrical pressure: their presence indicates defective design of the machine. This form of generator is known as the direct-current generator, and is the one necessary to use for electro-chemical work of the electrolysis type, and for storing energy in "storage batteries;" as well as being appropriate for lighting purposes and for driving electric motors.

A direct-current generator furnishing its own magnetism is called a "self-excited" generator. The pressure of the generator drives the

current through the coils on the electro-magnet marked " shunt field coils " in Figs. 94, 95, and 96. After the generator has been once used a certain portion of the magnetism remains in the magnet, after the current in the coils is turned off, and is known as " residual magnetism." This is used to build up the necessary magnetic field when the generator is used again. The voltage of a generator can be varied through the use of a variable resistance known as a " field rheostat," Fig. 94 or 95. By putting more resistance in the shunt field circuit the current decreases in these coils, thus decreasing the magnetism and therefore the voltage.

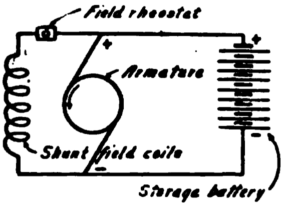


FIG. 94.

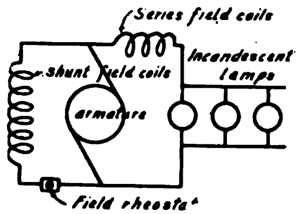


FIG. 95.

The two forms of direct-current generators in common use are the " shunt " and the " compound " generators. The electrical pressure of the former is considerably less at full load than with a small load, due to the resistance of the armature coils, which cause a drop in electrical pressure that increases directly as the current flowing. On account of this variation of pressure according to the load the shunt generator is limited in its use to charging storage batteries, and for certain electro-chemical processes where a reasonable variation of voltage is not objection-

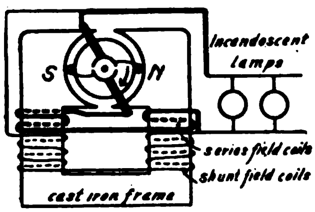


FIG. 96.

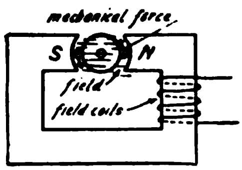


FIG. 97.

able. An electrical diagram is given in Fig. 94. For incandescent lighting and for driving electric motors as small a variation as possible in electrical pressure is desired. The compound generator keeps the voltage up as the current or load increases, by having a few additional turns of wire around the magnet frame that are in series with the armature (" series field coils "). This is indicated in Fig. 96, and also shown in the electrical diagram, Fig. 95. The current in the outside circuit increases with the load, and therefore the magnetism increases due to the series field coils, which increases the voltage accordingly. The voltage can in this way not only be kept

practically constant with a varying load, but can be increased with the load by adding more series field turns. The compound generator is the one used almost universally in power plants supplying direct current.

The Electric Motor. In order to convert electrical energy into mechanical energy for driving machinery, an "electric motor" must be used. A motor is similar in general construction to an electric generator. An electro-magnet forms the frame of the machine, and the revolving drum or armature is identical in construction with the armature of a generator. Fig. 97 gives the simplest form of an electric motor. A conductor on the right-hand side of the drum, and with a current passing through it, is forced out of the magnetic field in the direction indicated by the arrow. If the current is made to flow in the conductor in the opposite direction the mechanical force will be downward in place of upward, as shown on the left-hand side of the armature. This fundamental principle of a conductor, with a current passing through it, being forced out of a magnetic field is the basis upon which all electric motors operate. The turning force of the motor is increased by having a larger number of conductors on the circumference of the armature. The current gets into the revolving conductors in the same way as in the generator, through the stationary brushes resting on the revolving commutator. The motor being similar in mechanical construction to the generator, an electric motor can in general be used as a generator, by supplying mechanical power to the pulley and taking electrical energy from the armature.

Electrical measuring instruments use the same fundamental principle in their operation as electric motors, and are practically small electric motors. The direction of deflection of the needle of an electrical measuring instrument, or the direction of rotation of the armature of a motor, can be changed by reversing the direction of the current in the armature.

This principle of the electric motor also explains why the output of a generator increases directly with the increase of current, with a given electrical pressure (volts × amperes = watts). The greater the number of incandescent lights turned on in parallel, Fig. 98, the less the resistance of the circuit as a whole, and the greater the current; each 16 candle-power light adding one-half an ampere to the current in the main circuit and generator armature. This current in the conductors on the armature of the generator, in the magnetic field, tends, according to this motor action, to drive the armature of the generator in opposition to the prime mover. The greater the number of incandescent lights turned on the more steam required for the engine to keep the generator armature at the constant speed which is required to give a constant voltage. With no lights turned

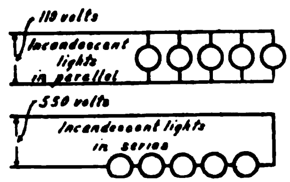


FIG. 98.

on there is no current in the armature of the generator, and being no current there is no turning force acting in opposition to the steam engine, except the mechanical friction of the bearings and brushes; this being known as the condition of no load previously referred to.

Electric Heating and Electric Furnaces. After the power is transmitted electrically it may be converted into mechanical energy by means of an electric motor, or it may be used directly to produce heat or to change chemical compounds into other compounds or break them up into elements—electric lighting and electric furnace work being examples of the former, and electrolysis of the latter. Why heat is produced by an electric current flowing through matter, or why the electric current has this chemical effect on compounds, is not known; it is known, however, that the quantity of heat produced depends upon the square of the current times the resistance of the conductor. In the case of the incandescent light with a current of $\frac{1}{2}$ ampere and a resistance of 220 ohms, the quantity of heat produced is represented by the square of $\frac{1}{2}$ multiplied by 220. This gives 55 watts. The same result is obtained by multiplying the volts by the amperes. The incandescent light is a simple resistance furnace, the manufacture of carborundum being an example of this type of furnace on a larger scale. The ordinary arc light is another form of electric furnace, in which the conductor consists of carbon particles or vapor in place of a solid conductor, the calcium carbide furnace being an example of this type on a larger scale. An electric arc has an electrical back pressure produced in the arc, so that the simple fundamental law $\text{amperes} = \frac{\text{volts}}{\text{ohms}}$ does not hold true for an arc furnace. The back pressure in an electric arc varies with the material used for the solid conductors at the ends of the arc. For carbon terminals, and material used in arc furnaces, this back pressure is about from 30 to 40 volts, so that it is impossible to operate an arc furnace at an electrical pressure less than this voltage. For instance, 50 volts is applied to an electric arc furnace, giving 2000 amperes flowing through the furnace; the actual electrical resistance of the furnace, assuming the electrical back pressure to be 35 volts, will be $\frac{50-35}{2000} = 0.0075$ ohms$\left(\frac{\text{voltage}}{\text{current}} = \text{resistance}\right)$. The power put into this furnace is the pressure applied times the current flowing $= 50 \times 2000 = 100{,}000$ watts $= 100$ kilowatts, so that the generator supplying this power would need to be of 100 kilowatt capacity, and of 50 volts pressure. Either direct-current or alternating-current furnaces can be used; and the same is true for simple resistance furnaces, an incandescent lamp, of course, working the same on an alternating-current as on a direct-current circuit. The voltage used for a simple resistance furnace, such as in the manufacture of carborundum, depends upon the length and area of cross-section of the path of the current, and upon the nature of the material through which the current passes. About 80 volts is the pressure applied

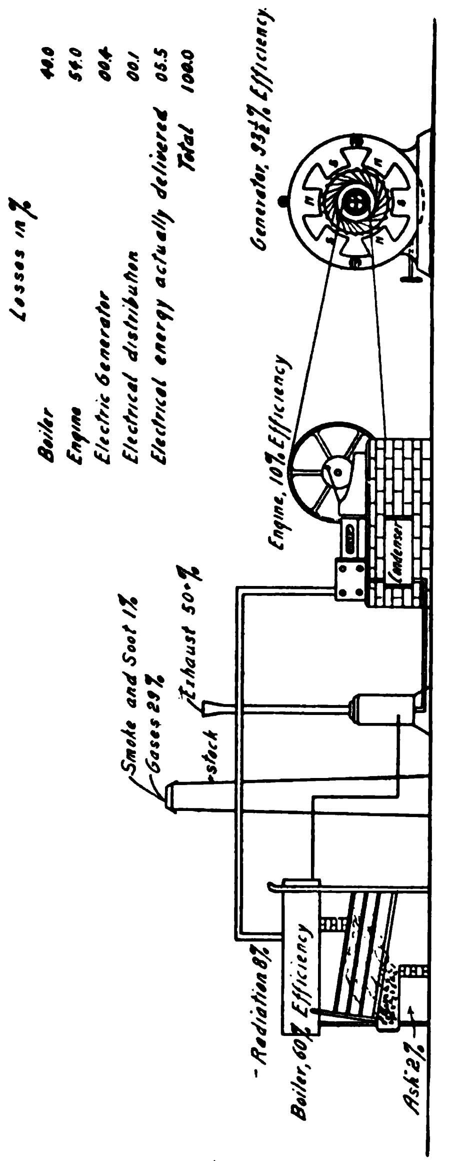
to the carborundum furnace after it gets to its full temperature. A 100 kilowatt furnace would have $\frac{100,000}{80}=1250$ amperes flowing through it.

The heating effect of the current passing through a conductor is made use of in electric cooking and electric heating apparatus. Such apparatus consists usually of a metallic frame in which coils of wire (copper, iron, or German silver,), are embedded in enamel, that protects the coils as well as insulating them. The length and cross-section of this wire offers the resistance that, with a given electrical pressure, allows the quantity of current to flow so as to produce the temperature required. The cleanliness and convenience of electric cooking and heating apparatus for many purposes offset the increase in cost of their operation. An electric heater converts all of the electrical energy into heat. The loss is not in the heater itself, but in the inefficient methods of changing the energy of the fuel into electrical energy. This is indicated in the diagram of losses, Fig. 99. It will be seen that from 5 to 6 per cent only of the energy of the fuel is available for distribution to the electric heaters, and hence it pays to obtain the heat from the fuel directly. Also it will be noticed that a large proportion of the heat units of the fuel are wasted in the exhaust steam from the engine, and it is for this reason that it pays to use the exhaust steam from the engines of the power house for heating purposes, wherever possible. Water-power plants do not, in general, produce electric energy at a much lower cost than steam plants, because the interest on the capital invested in the necessary water-power improvements frequently offsets the cost of coal for the steam plant. Water-power development, however, is a better financial proposition in many parts of the country where the price of coal is high.

In a motor or generator the heating effect of the electric current is of disadvantage, as it limits the output. The full load current of either a generator or motor brings the conductors on the armature to about 40° C. above the surrounding air. Beyond this temperature the cotton insulation around the conductors deteriorates. Over 25 per cent overload current will char the insulation, and the armature will burn out and must be rewound. Care must be taken that the load applied to either a generator or motor does exceed full-load current. To guard against excessive currents due to either accident or overload, a "fuse" is placed in series with each wire. These fuses consist of strips of soft metal that melt or "blow" when too large a current flows, thus opening the circuit so that no more current can flow. All generators and motors are protected by fuses, and in many cases also by "circuit breakers" (mechanical devices for opening the circuit).

Losses in Electrical Transmission. The higher the electrical pressure used in transmitting a given amount of power the less will be the current flowing in the wire, and consequently the loss of energy by the heat produced by the current will be diminished. The current also causes a

drop in electrical pressure along the wire, that is equal to the current times the resistance of the wire. The electrical pressure at the end of a transmission line is therefore less than it is at the power house, the allowable drop in standard transmission systems being from



TRANSFER OF ENERGY FROM THE FUEL TO ELECTRICAL ENERGY.
(About 5½% only of the energy of the fuel obtained from the Generator)

FIG. 99.

5 to 10 per cent of the voltage used in transmitting the power. It is thus necessary to have either a small current or a small resistance in the wire in order to reduce the loss in heat and drop in pressure to a minimum. A small resistance requires a large cross-section of copper, which

makes the first cost of the copper wire excessive. Hence a high potential with its corresponding small current is essential. In order, therefore, to reduce the outlay of capital for the transmission line high voltages are used for long-distance power transmission.

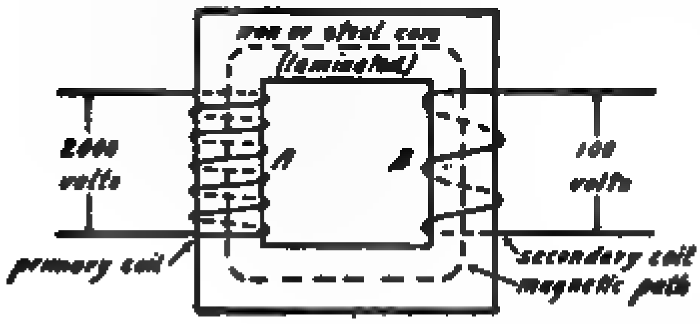


FIG. 100.

Transformers. Of the two systems, alternating and direct current, the alternating current is used almost entirely for long-distance power transmission. Some special systems in Europe are exceptions to this general rule. We have no economical means of converting a high direct-current voltage to a low direct-current voltage, which is needed after the power is transmitted. Whereas an alternating pressure can readily be changed from a higher to a lower pressure by means of what is called

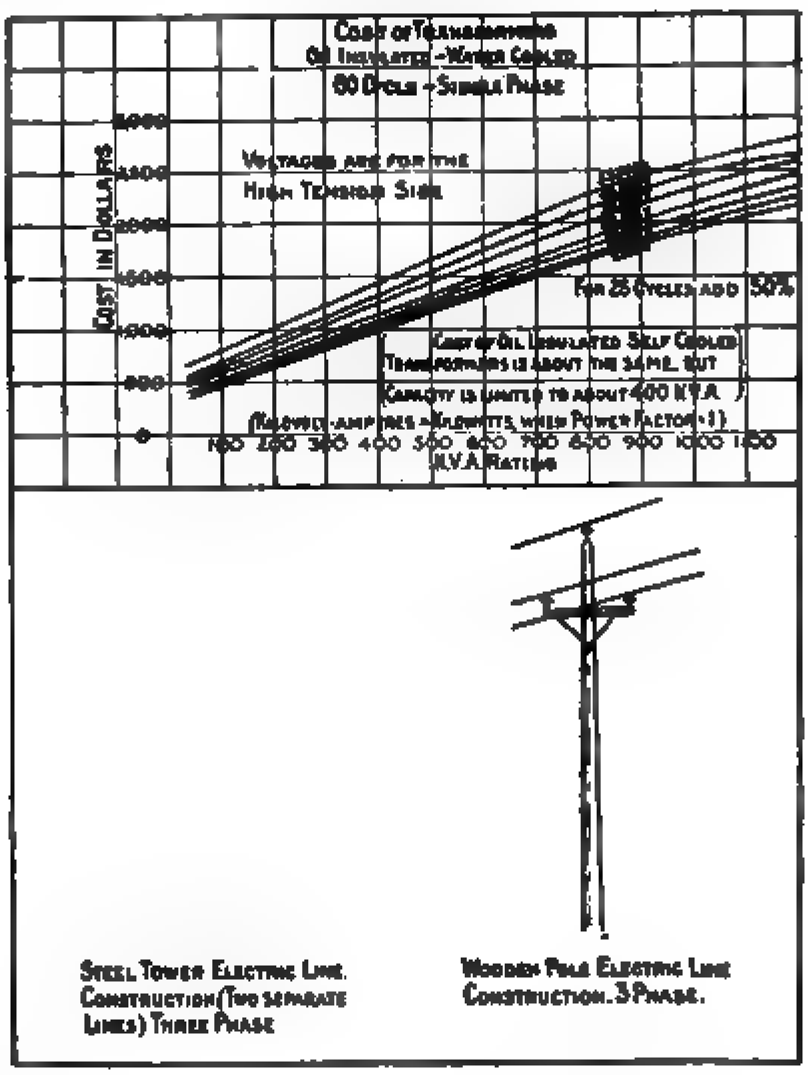


FIG. 101.

a " transformer." The operation of a transformer is based upon the well-known fact that whenever magnetism changes within a coil of wire an electrical pressure is produced in the coil. Referring to Fig. 100, coil *A* is wound around an iron core, and having 2000 volts alternating pressure applied to this coil the resulting alternating current produces an alternating

magnetism in the iron core and within coil B. This changing magnetism within coil B produces an alternating electrical pressure at the terminals of the coil that is directly proportional to the number of turns of wire in the coil. With double the number of turns in coil B, the electrical pressure of that coil is doubled. There is no limit to the voltage that can be obtained from this secondary coil, B, except that there is a practical limit to the insulation that will withstand the strain of a very high voltage. An electrical pressure of 138,500 volts is the highest voltage in continuous use at present. A high voltage from the secondary does not mean an increase of power, because power is equal to volts times amperes, and the power output of a transformer cannot, of course, be greater than the

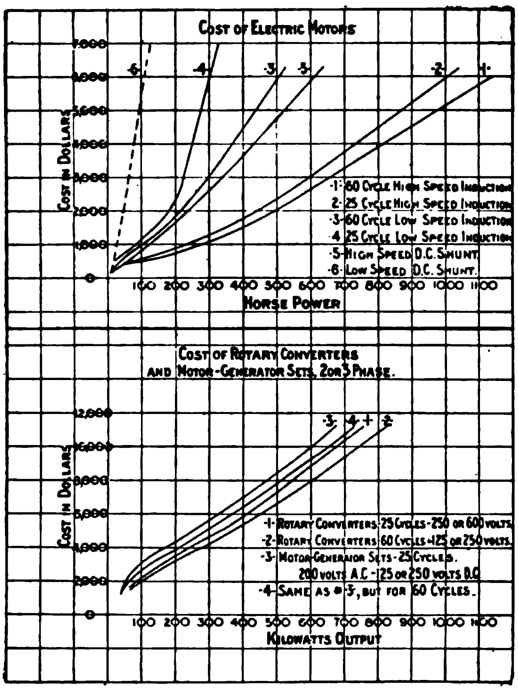


FIG. 102.

power input; so that a high voltage means a correspondingly low current in the coil. When used to change from a low to a high alternating pressure the transformer is known as a " step-up " transformer, and when used to pass from a high to a low pressure is called a " step-down " transformer.

Such a piece of apparatus as this has about 98 per cent efficiency at full load, and costs from \$2 to \$8 per kilowatt capacity, Fig. 101. There being no moving parts in a transformer no regular attendance is required on the part of an operator. To get from one direct-current voltage to another it is necessary to use a direct-current motor driving a direct-current generator giving the desired voltage; this combination being called a " motor-generator " set, and costing from \$15 to \$25 per

kilowatt capacity, with an efficiency of from 75 to 85 per cent. To get from an alternating pressure to a direct-current pressure a motor-generator set can be used; that is, an alternating-current motor in this case driving a direct-current generator. A " rotary converter " may be used for this purpose also, the same being an alternating-current motor and a direct-current generator combined in one machine. The first cost is somewhat less in this case than for a motor-generator set, and the efficiency is about 10 per cent higher (Figs. 102 and 103). Rotary converters are used at the delivering end of a power transmission line for obtaining the 550 volts usually employed for street railway systems, and for getting direct

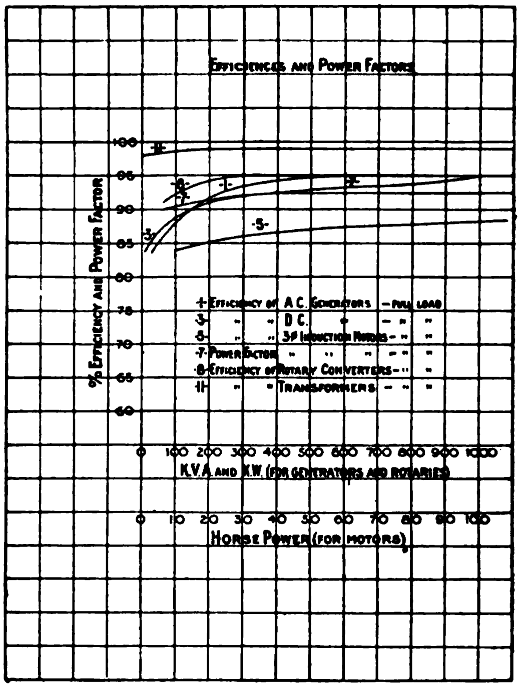


FIG. 103.

current for certain electro-chemical industries. A simple sketch of a high-voltage transmission system is shown in Fig. 104, the alternating-current generator's voltage of about 2200 volts being transformed up to 33,000 volts, and at the delivering end of the line. The pressure is reduced to 30,000 volts on account of the drop in pressure along the wires. This is transformed to 550 volts, and the 550 volts drives an alternating-current motor which is connected to a direct-current generator giving 110 volts, or whatever direct-current pressure is desired: upon the same line another transformer may supply 110 volts alternating pressure for lights.

Polyphase Systems. The alternating-current system is the standard for power transmission in this country. To save in copper for trans-

mission lines, and to decrease the first cost of electrical machinery, what are known as "polyphase" systems (two- or three-phase) have been developed. The ordinary two-wire alternating-current circuit is what is called a single-phase circuit, one voltage being obtained between the two wires. A "two-phase" circuit has two different voltages—one developed by coil A on the armature of the simple generator shown in Fig. 105, and the other developed by coil B on the armature. These two voltages A and B are each single-phase voltages, but differ in that the volt-

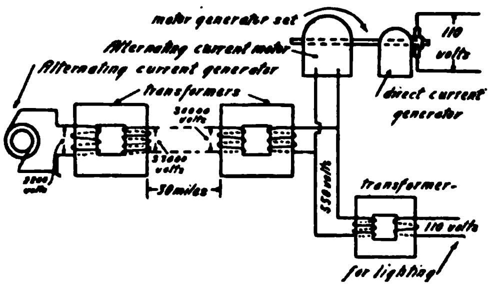


Fig. 104.

age of B is at a maximum when the voltage of A is zero, and vice versa; that is, the voltage of B is 90° ahead of that of A. If in place of four wires coming from the generator, each carrying a current of 100 amperes, coils A and B are connected together as shown in Fig. 106, the resultant current flowing in the middle wire X is equal to the diagonal of the square (the current of phase A being 90° from current in phase B), and in actual value equal to $\sqrt{2}\times100$ amperes. In other words, in place of having two wires each carrying 100 amperes, one wire can be used carry-

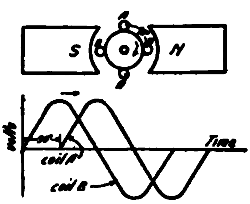


Fig. 105.

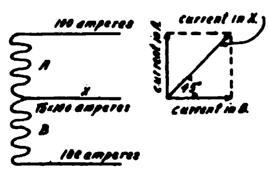
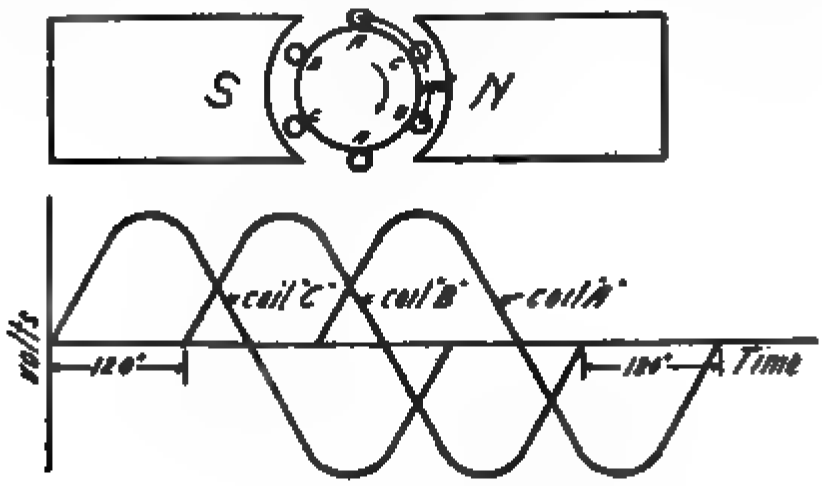


Fig. 106.

ing 141 amperes, requiring less cross-section of copper conductor, and therefore less cost for the wire. This combination of currents differing in phase from one another, giving less current in one wire than in two separate wires, is the reason in general why polyphase systems require less copper in the transmission wires as well as in the armatures of generators and motors. A three-phase circuit has three different voltages, each 120° from the other, as indicated in Figs. 107 and 108, the three coils being connected together so as to use three wires running from the generator in place of six, the combination of currents 120° apart reducing still more the necessary cross-section of the copper wire. The three coils in three-phase motors

are placed in the same relative positions as indicated on the armature of the generator. For power transmission three-phase is the standard system, although the two-phase system is simpler in construction. To get the maximum output of a polyphase generator the system should be " balanced "; that is, each coil of the generator armature should have the same



Simple Three Phase Generator

FIG. 107.

power output and equal current. If one phase has more current than the others that winding may be burned out in order to get the full rated output of the generator, with the other two phases underloaded: so that in practice it is planned to keep the system as nearly balanced as possible. Single-phase can be obtained from any polyphase circuit, from any two of the

Three Phase Transmission System

FIG. 108.

wires, such as for lighting incandescent lights. In this case an equal number of lights should be placed between each two of the three wires of the three-phase system, in order to keep the system balanced.

Power in Alternating-current Circuits. The power output of a single-phase generator is = volts × amperes × " power-factor." For incandescent lights the power factor is 1.00, and for the most common type of

alternating-current motors the power-factor is given in Fig. 103. With a mixed load of lights and motors, the power-factor will vary, depending upon the relative proportion of the power for the motors and for the lights. With lighting transformers at the average load, the power-factor is about 0.96, and for "induction motors" alone about 0.80 as a conservative figure for the average loads met with in practice. Within these limits will be found the power-factor for most transmission systems. For a two-phase three-wire system the power is $= \sqrt{2} \times$ volts (between the center and outside wire) $\times$ amperes in the middle wire $\times$ power-factor. The current in either outside wire is the current in thec enter wire divided by the $\sqrt{2}$,

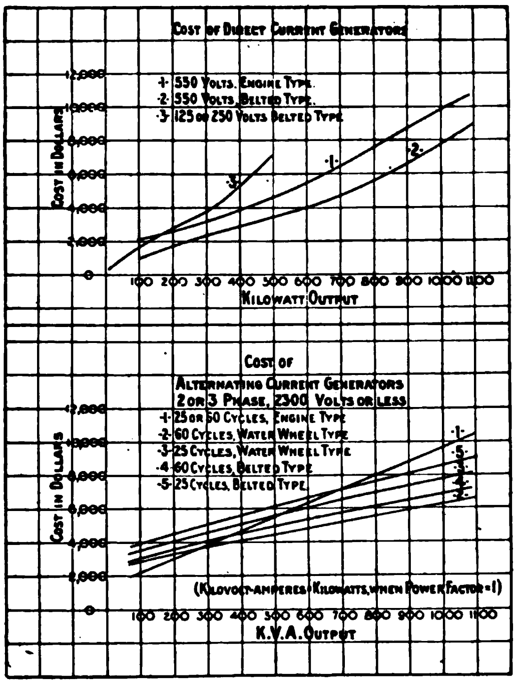


FIG. 109

for a balanced system. For a three-phase system the power $= \sqrt{3} \times$ volts between any two of the three wires $\times$ the current flowing in any one of the three wires $\times$ power-factor.

Size of Wire Required for a Given Electric Motor. The following problem will give a general idea of how to calculate the size of wire necessary to run to a motor of given output.

It is desired to install a 100 horse-power, 550-volt motor in a mill for driving the main-line shafting. Assuming the efficiency of the motor to be 91.5 per cent, (*A*) What size of wire will be required if the motor is to be a direct-current motor? (*B*) What size of wire will be required if the motor is to be a three-phase induction motor, assuming a power-factor of 0.94 at full load?

(*A*) 100 horse-power $=100\times746=74{,}600$ watts. Power in a direct current circuit = pressure $\times$ current $=74{,}600$; current $=\dfrac{74{,}600}{550\times(\text{eff.}=0.915)}$ $=148$ amperes. So that each of the two wires must carry 148 amperes; and this, according to the insurance regulations, requires a number 00 wire, as shown by the table at the end of this chapter (rubber-covered wire, interior use).

(*B*) If a three-phase motor: $74.600=\sqrt{3}\times\text{volts}\times\text{amperes}\times\text{power-factor}=\sqrt{3}\times550\times\text{current}\times0.90$; so that the current in each of the three wires is $=\dfrac{74{,}600}{\sqrt{3}\times550\times0.94\times0.915\ (\text{eff.})}=91$ amperes; which means that running to the motor there must be three No. 2 wires (as found from the table at the end of this chapter). A 100 horse-power motor is supposed to deliver 100 horse-power; the wires must carry the power lost in the motor as well as the power delivered, hence the efficiency is put into the denominator of the above equations. It will be noticed, from the wire table, that three No. 2 wires weigh less than two No. 00, for a given distance; so that there is less cost for the wires running to the three-phase alternating-current motor than for the direct-current motor. Any number of motors may be placed on the same circuit (in parallel), the total horse-power of the motors in that case being used in the calculations for finding the necessary size of wire.

In finding the size of wire for a given number of incandescent lights, the length of wire for a long mill or factory may be so great as to give more than 2 per cent drop in voltage along the wires, for the size required by insurance regulations for a given current. In this case, either larger wire should be used to decrease the voltage drop, or lower voltage lights ought to be used at the part of the line farther away from the generator. Incandescent lights for this purpose can be purchased for different voltages, such as from 100 to 120 volts, their rated voltage being required to give the full candle power of the lamp. To get the drop in electrical pressure in volts, multiply the current flowing in the wire by the resistance of the wire to and from the lights, the resistance of the wire for a given size being found from the table. A general rule to keep in mind for all cases is that the most economical size of conductor is the one with such a resistance that the cost of the power lost in heat is equal to the interest on the original cost of the conductor.

Types of Electric Motors. Where the power transmitted is to be converted into mechanical power by means of electric motors, it is essential to have at least a general knowledge of the different types of motors. Alternating-current motors get their power directly from transformers at the delivering end of the transmission line. Direct-current motors must be used on direct-current systems. Direct-current power can be obtained from an alternating-current system through the use of a rotary converter

changing from the alternating- to the direct-current system. Electric motors may be classified as follows:

ALTERNATING-CURRENT MOTORS

Induction Motors

1. Slight variation in speed from no load to full load.
2. Two- and three-phase induction motors are self-starting, with reasonable load.
3. For small sizes, particularly up to about 100 horse-power, the induction motor is the alternating motor used almost universally.
4. Induction motors are simple in their construction and operation, and require only a simple starting device.

Synchronous Motors

1. Run at perfectly constant speed from no load to full load.
2. Not self-starting; some auxiliary means must be used to get the synchronous motor at full speed before the electrical pressure is applied to the armature.
3. Used in large sizes where the motor is to run more or less continuously.
4. In general, the synchronous motor is an alternating-current generator operated as a motor, requiring a small direct-current generator, called an exciter, to supply the constant magnetism

DIRECT-CURRENT MOTORS

Shunt Motors

1. Slight variation in speed from no load to full load.
2. This motor is used in almost every case where nearly constant speed is required, such as for driving the main-line shafting in factories, etc.

Compound Motors

1. Greater variation in speed than in the shunt motor, but giving a greater driving force. Used in cases where sudden overload comes on the motor, such as for running a press, for punching steel, also where a very heavy starting force is required.
2. Cost about the same as shunt motors.

Both shunt and compound motors may be used as generators, the compound machine giving a constant, or a slight increase, of voltage with increase of load, and the shunt generator giving considerable decrease in voltage with increase of load. For direct-current lighting systems, as well as for driving motors requiring constant voltage near the power station, compound generators should be purchased; shunt generators are used only for special purposes. For distances beyond several hundred feet an alternating current system of 2200 volts or more should be installed to keep the cost of the copper wires within a reasonable figure, and transformers used

to bring the pressure down at the end of the line from 2200 volts to the desired pressure for lights or motors.

Loss in Pressure along a Transmission Line. A three-phase power transmission system has three wires on the pole line, or in some cases two separate lines of three wires each, as indicated in Fig. 101, each wire carrying the same current if the system is balanced, as is planned for as far as possible (three-phase motors form a balanced load). In an alternating current system the drop in pressure along the line is due chiefly to the electrical resistance of the wire; there is another item called " inductance " that causes an additional drop in pressure; the combination of resistance and inductance is called the " impedance " of the circuit or line. The inductance of a transmission line depends upon the distance apart between the wires, and the length of the line, making the impedance increase somewhat with the increase of distance between the wires. The table at the end of this chapter gives both the resistance of the wire per mile of one wire, and the impedance in terms of per mile of copper wire with the different standard distances between wires. The distance between wires is increased with the increase of electrical pressure used, in order to prevent the current from leaking from one wire to another through the moisture of the air. The drop in electrical pressure due to the current flowing in the wires of a three-phase system, between any two of the wires, is equal to the total impedance of one of the wires (as given in the tables) multiplied by the current in that wire and also by the $\sqrt{3}$. For a single-phase alternating-current circuit, the drop in pressure between any two of the wires is the current of one wire, multiplied by the impedance of that wire, times 2: in a direct-current circuit the resistance and impedance are the same, and for interior wiring they are practically the same for alternating-current circuits on account of the wires being but a short distance apart.

The following problem illustrates the application of the principles taken up in this chapter, as well as serving as a guide for the calculations for any case of the electrical transmission of power:

A new cotton mill will require 1500 horse-power delivered to the mill, for driving machinery and for lighting purposes, ten hours per day. Twenty miles from the mill there is a water-fall with a 50-ft. effective head and with a guaranteed development of 3000 horse-power, as determined by the measurements of a civil engineer. It is estimated that the water-power improvements, including the cost of construction of the dam, will amount to \$155,000. Will it pay to develop this water-power and transmit the power electrically? Will it be better economy to erect a steam plant at the mill, coal costing \$3.40 a ton of 2000 pounds delivered? Will a gas-producer plant be more economical? In all three cases it is assumed that the power is taken into the mill electrically, and that the groups of machines are driven by individual motors. This use of individual motors in place of having a shaft running directly into the mill from the power plant is common practice. The shafting with its belts, bearings, and pulleys, takes up space as well as interfering with the proper distribution of light for efficient labor service.

WATER-POWER PLANT

Cost of water-power improvements, including dam	$155,000.00
Three 700-H.P. water turbines (see Fig. 88)	8,200.00
Hydraulic fittings, general figure, $4.00 per H.P.	8,400.00
Three 500-K.W., three-phase, A.C. generators, 2200 volts, (see Fig. 110)	13,500.00
Switchboard equipment, wiring, etc., general figure, $6.00 per K.W.	9,000.00
Three direct-current generators for exciters, to supply the magnetism for the alternators, each of about 4 per cent of the capacity of each alternator; making 60 K.W. total (see Fig. 110) ($25 per K.W.)	1,500.00
"Step up" transformers; two banks of three single-phase transformers each; each transformer of 250 K.W. capacity, and transforming from the 2200 volts of the generators to 22,000 volts for transmission. 60-cycle, oil-insulated self-cooled (see Fig. 102)	5,280.00
Complete cost of pole line, exclusive of the wire used, varies from $400 to $1500 per mile, depending upon the locality, kind of poles and insulators, and the nature of the ground for setting the poles. Assuming $800 per mile in this case (including little or no cost for the "right of way") 20 miles	16,000.00
Two banks of "step down" transformers, 60-cycle, oil-insulated, self-cooled, making six of about 225 K.W. capacity; and transforming from 20,400 volts to 550 volts for motors, and through a second bank of transformers to 110 volts for the lights (see Fig. 102)	4,800.00
Copper conductors for three-phase line, assuming copper to be 15 cts. per pound	7,700.00
	229,380.00

Interest on this amount at 5 per cent $11,469.00
Operating costs: labor, $10.00 per day .... $3,100.00 per year.

In general, 1000 volts per mile for an electrical pressure is allowed as a starting point to determine the necessary size of copper wire; but as both the amount of power and the distance of transmission determine the voltage to be used, the final result may show a higher or lower voltage than that originally assumed. The general standard high voltages are as follows: 2200, 4400, 6600, 13,200 (about the maximum to get directly from the generator, it being more economical to get higher voltages by means of transformers) 22,000, 33,000, 44,000, 66,000, 88,000, 110,000, 138,500, the latter being extreme, and the highest voltage in practical use at this time. Assuming 22,000 volts in this case, a power factor of 0.92 (for motor loads, induction motors averaging about 125 H.P. and one synchronous motor, and smaller load of lights), and an allowable drop in voltage along the line of 8 per cent; the voltage at the delivering end of the line would be about 20,400 volts, with 22,000 volts at the power station. The power in a three-phase system $= \sqrt{3} \times$ pressure $\times$ current $\times$ power-factor $= \sqrt{3} \times 20{,}400 \times$ current $\times 0.92 =$ delivered power $= 1538$ (H.P.) $\times 746 =$ the power to be delivered to the transformers at the mill (allowing 2.5 per cent average loss in the step down transformers). Solving for the current in this equation $= (1538 \times 746) \div (\sqrt{3} \times 20{,}400 \times 0.92)$ $= 35.3$ amperes as the current flowing in each of the three wires. The voltage drop between any two of the wires (8 per cent) is about 1600 volts ($22{,}000 - 20{,}400$); dividing this by the $\sqrt{3}$, gives the voltage drop in terms of one wire $= 926$ volts. As part of the power transmitted is to be used for lighting purposes, 60 cycles frequency would be used. With the wires 36 ins. apart (this distance is increased with the voltage used, depending somewhat upon the locality or the dampness of the atmosphere at any season) the impedance per mile in terms of one wire would be

(total volts drop) ÷ (current × miles) = 926 ÷ (35.3 × 20) = 1.31 ohms. This corresponds, according to the table at the end of this chapter, to a No. 3 wire (with 60 cycles), 1.258 being the actual impedance per mile for this size wire, that of No. 4 being too great. Bare wire is used for high voltage transmission lines. No. 8 is about the smallest size used for outdoor work, sleet and ice in northern climates adding too much weight for smaller wire: for reliable long-distance transmission lines nothing smaller than No. 5 wire should be used, on account of the mechanical strength.

With copper at 15 cents per pound, the cost of the three wires in this case, 20 miles, 5280 ft. per mile, and No. 3 wire weighing 159.38 pounds per 1000 ft. (see table), is $3 \times 20 \times 5280 \times 0.15$ = \$7700 (about). By using the next higher standard pressure, the size of the wire would be too small, for mechanical reasons. If the next smaller standard voltage were used, the increase in the cost of the copper wire would be found to exceed the decrease in the cost for lower voltage transformers, and slight decrease in cost of pole line for lower voltage. The higher the cost of copper, the greater the saving in using a higher voltage to bring the size of wire down to the smallest advisable for mechanical strength; but the higher the voltage the less reliable the system may be in damp atmospheres, particularly above 44,000 volts.

In cases where there is no power to spare, and where there is plenty of capital available, the general rule should be applied, that the most economical size of conductor is the one with such a resistance that the cost of the power per year lost in heating the wires is equal to the interest per year on the original cost of the conductor. Applying this rule to the present case: the interest on the cost of the conductors (5 per cent) is \$385; about 82 K.W. (7 to 8 per cent) being lost along the line, at a cost of about \$5.75 a day at the power station (about 0.7 cent per K.W. hour), gives a cost for the power lost per year of about \$1775. But if there is no further market for the spare power, in this case, the power lost is really worth less than the above figure. Where advisable, either the size of the wire could be increased, or 30,000 volts used in place of 20,000, to decrease the cost of the power lost.

STEAM-POWER PLANT

Three compound condensing slow-speed engines, of 550 B.H.P. each (see Fig. 81)		\$37,500.00
Cost of auxiliaries, average \$8.00 per H.P.		13,200.00
Cost of fire-tube boilers, six 200 H.P. (Fig. 81)		8,500.00
Three alternating current generators, 400 K.W. each (550 volt generators, no transformers being necessary), (see Fig. 110)		14,450.00
Three 16-K.W. direct-current generators for exciters, to supply the magnetism for the alternating-current generators (see Fig. 110)		1,250.00
Switchboard equipment, \$4.00 per K.W.		4,800.00
Cost of stack or chimney at \$3.25 per H.P.		5,400.00
Total		85,100.00
Interest on this amount at 5 per cent	\$4,255.00	
Operating expenses: 7620 tons of coal per year, of 308 ten-hour days, for 1650 H.P. at a coal consumption of 3 lbs. per B.H.P. per hour for this type of engine (see Fig. 85)		25,920.00
Labor as in the water-power plant		3,100.00
Additional labor over what would be necessary in the water-power station: three firemen at \$1.75 each per day		1,600.00
Total operating costs		\$30,620.00

GAS-PRODUCER PLANT

Three 600-H.P. gas engines with gas-producers and accessories (see Fig. 88)		$105,000.00
Three 400-K.W. alternating-current generators, 550 volts (Fig. 110)		14,450.00
Three 16-K.W. exciters (Fig. 110)		1,250.00
Switchboard equipment, $4.00 per kilowatt		4,800.00
Total		$125,500.00
Interest on this amount at 5 per cent	$6,275.00	
Operating expenses: 2800 tons of coal per year of 308 ten-hour days. 1650 H.P., coal $3.40 per ton. 1.1 lbs. per B.H.P. (see Fig. 88)		9,500.00
Labor as in the water-power plant		3,100.00
Additional labor over what would be necessary in the water-power station; two men at $1.75 per day		1,100.00
Total		$13,700.00

Comparing these three plants:

Plant.	Capital Costs.	Fixed Charges (Interest, Depreciation, Taxes, Insurance, etc.) 5% + 10%.	Operating Expenses. (Fuel, Labor, Supplies.)	Cost per Year (Fixed Charges Plus Operating Expenses).
Water-power plant	$229,380.00	$11,469 + 8500 = 19,969.00 (10% on machinery and pole line only)	$ 3,100.00	$23,069.00
Steam plant	85,100.00	4,255 + 8,510 = $12,765.00	30,620.00	43,385.00
Gas-producer plant	125,500.00	6,275 + 12,500 = $18,775.00	13,700.00	32,475.00

It may be noted that the interest on the initial cost of the water-power plant about offsets the cost of coal per year for the steam plant; and in localities where coal is comparatively cheap, and the cost of the water-power development high, the steam-plant development may be better economy.

The yearly cost of power per K.W.-hour is obtained by dividing the total cost per year, as tabulated, by the number of K.W.-hours actually used during the year. The number of hours of operation per year, of 308 ten-hour days, would be $308 \times 10 = 3080$ hours; and multiplying this by the number of K.W. output of the plant, the following costs per K.W.-hour are obtained for the power delivered:

Plant.	Yearly Cost.	K.W.-hours per Year.	Cost per K.W.-hour.
Water-power plant	$23,069.00	3,450,000	0.67c.
Steam-power plant	43,385.00	3,450,000	1.26c.
Gas-producer power plant	32,475.00	3,450,000	0.94c.

Cost of construction of each plant, *per horse-power output*, (not including cost of land or buildings, or cost of pole line)	Water-power plant	$100.00
	Steam-power plant	52.00
	Gas-producer plant,	75.00

From the preceding figures it will be seen that the water-power plant seems to be the most appropriate for this case. Taking into account the

particular locality, the cost of land and buildings, and other items affecting the costs beyond general conditions, might show a different result. It is at this stage that the good or bad judgment of the engineer comes in. It must be remembered that these are general considerations and general costs only, showing the principles involved, the final decision being made after actual quotations are obtained, and all items considered in detail.

STANDARD WIRE TABLE (COPPER)

Size of Wire B. & S. Gauge.	Diameter in Inches (Bare).	Distance between Centers of Wires.	Resistance per Mile of One Wire.	Impedance per Mile of One Wire. 60 Cycles.	Impedance per Mile of One Wire. 25 Cycles.	Weight per 1000 Feet (Bare Wire).	Safe Current-carrying Capacity, Rubber-covered Wire (Interior Use).
		Inches.		Ohms.	Ohms.	Pounds.	Amperes.
16	0.051					7.82	6
15	0.057					9.86	8
14	0.064					12.44	12
13	0.072					15.68	14
12	0.081					19.77	17
11	0.091					24.93	21
10	0.102					31.44	24
9	0.114					39.65	29
8	0.128	24	3.280	3.362	3.294	49.99	33
8	0.128	36		3.375	3.296		
8	0.128	48		3.385	3.298		
8	0.128	60		3.392	3.299		
8	0.128	84		3.405	3.301		
7	0.144	24	2.590	2.694	2.607	63.03	39
		36		2.707	2.609		
		48		2.717	2.611		
		60		2.725	2.613		
		84		2.738	2.615		
6	0.162	24	2.045	2.166	2.067	79.49	45
		36		2.184	2.070		
		48		2.196	2.072		
		60		2.206	2.074		
		84		2.221	2.077		
5	0.182	24	1.624	1.772	1.650	100.23	54
		36		1.791	1.653		
		48		1.808	1.656		
		60		1.819	1.658		
		84		1.838	1.661		
4	0.204	24	1.290	1.464	1.322	126.40	65
		36		1.489	1.328		
		48		1.505	1.330		
		60		1.520	1.333		
		84		1.541	1.338		
3	0.229	24	1.025	1.229	1.063	159.38	76
		36		1.258	1.069		
		48		1.278	1.075		
		60		1.294	1.078		
		84		1.318	1.082		
2	0.258	24	0.808	1.046	0.854	200.98	90
		36		1.078	0.861		
		48		1.113	0.866		
		60		1.120	0.870		
		84		1.149	0.877		

STANDARD WIRE TABLE (COPPER).—*Continued.*

Size of Wire B. & S. Gauge.	Diameter in Inches (Bare)	Distance between Centers of Wires.	Resistance per Mile of One Wire.	Impedance per Mile of One Wire, 60 Cycles.	Impedance per Mile of One Wire. 25 Cycles.	Weight per 1000 Feet (Bare Wire).	Safe Current-carrying Capacity, Rubber-covered Wire (Interior Use).
		Inches.		Ohms.	Ohms.	Pounds.	Amperes.
1	0.289	24	0.644	0.915	0.694	253.43	107
		36		0.951	0.707		
		48		0.977	0.713		
		60		0.998	0.718		
		84		1.029	0.726		
0	0.325	24	0.509	0.815	0.574	319.74	127
		36		0.853	0.583		
		48		0.882	0.591		
		60		0.904	0.596		
		84		0.938	0.605		
00	0.365	24	0.403	0.741	0.479	402.97	150
		36		0.784	0.491		
		48		0.813	0.499		
		60		0.837	0.506		
		84		0.873	0.516		
000	0.410	24	0.319	0.687	0.408	508.12	177
		36		0.731	0.421		
		48		0.763	0.430		
		60		0.787	0.438		
		84		0.825	0.450		
0000	0.460	24	0.254	0.646	0.355	640.73	210
		36		0.692	0.369		
		48		0.724	0.380		
		60		0.750	0.389		
		84		0.785	0.400		

No. 0000 wire is the largest size in the solid form, being about one-half inch in diameter; for a larger cross-section of copper, strands of wire are used in the form of a cable; sizes being given in " circular mils " rather than stated by numbers as above.

The cost of bare wire varies with the cost of copper at any particular time: and the price of rubber-covered wire as for interior use varies with the price of copper, rubber, and the size of wire, less weight of insulation per pound of copper being required for the larger sizes.

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VII

SULPHURIC ACID

WILLIAM M. GROSVENOR

Occurrence. Sulphuric acid is found in commerce as: Chamber acid (about 53° Bé., 66.6 per cent H_2SO_4) taken from the bottoms of the chambers in the chamber process; Glover acid (about 60° Bé., 77.7 per cent) taken from the first or Glover tower of the chamber process; 66 acid, is fairly pure acid concentrated (see p. 196) to 66° Bé., 93.2 per cent; 98 acid, of 98 per cent made by concentration or by the contact process (see p. 207) and generally of great purity; oleum or fuming acid (100 per cent H_2SO_4 containing additional SO_3 in solution) made by distillation of sulphates (obsolete) or by the contact process; Nordhausen acid (oleum when made from distillation of weathered shales (obsolete) containing iron sulphate or from $FeSO_4$) approximating a composition $H_2SO_4SO_3$ or $H_2S_2O_7$ which is pyrosulphuric acid; and oil of vitriol, also called o.v. (generally about 66°). The old name " oil of vitriol " is derived from its first preparation by the alchemists Gaber, Valentine and their predecessors who made it by distillation of sulphates, particularly green vitriol, $FeSO_4$, or by the burning of sulphur after the addition of saltpeter. In fact, historically, sulphuric acid is one of the first isolated acids, known to the Arabians in the eighth century and to Europe in the fourteenth and fifteenth centuries, when chemical industries really began to develop.

Industrial Position. The importance of an industry is something by which we should always be guided. The tonnage indicates to a great degree the opportunity for engineering skill; the value marks the utility of effort to improve (except revolutionary improvements that establish entirely new price levels and thereby new horizons of usefulness). There are something over 150 sulphuric acid plants[1] in the United States, the majority of the plants being located in Georgia, Pennsylvania, New Jersey, New York, South Carolina, Maryland and Ohio. Expressed in short tons (as 50°), the 1,869,000 tons production of 149 works in the United States in 1905 is distributed among North Atlantic States 768,000, South Atlantic 540,000, North Central 350,000, South Central 141,000

[1] For the European relations of the industry to alkali and muriatic acid manufacture (not so general in the United States) see Lunge, "Sulphuric Acid and Alkali," third edition.

and the Western, where mining and agriculture predominates, 69,000. One would, therefore, not consider a very large installation in the West without providing some new outlet, or in the East without preparing to meet competition. The value of the acid produced in the United States in 1905 was $15,174,886. Compared with other industries it is a grown man though by no means a giant. In tonnage it is less than half that of the salt production which is 2,901,506 tons, while it is considerably greater than news paper, 912,822 tons. Compared with other products generally known as chemicals it stands second to the greatest, fertilizers.

Nitric	54,190 tons		$5,232,527
Mixed	70,334 "		4,142,147
Muriatic	94,269 "	various strengths	1,730,231
Acetic	14,753 "		597,235
Boric	3,478 "		527,190
Sodas	734,209 "		13,357,983
Fertilizers	3,591,771 "		56,973,634

Uses of Sulphuric Acid. The principal uses of sulphuric acid are indicated, together with the quantity used calculated into tons of 50° Bé., 62.18 per cent, in the following table:

Fertilizer manufacture	803,358 tons
Petroleum purification	181,782 "
Pickling iron and steel	125,000 "
Alum manufacture	71,426 "
Mixed acid manufacture	63,059 "
Textile industry	50,000 "
Muriatic manufacture	48,750 "
Nitric manufacture	47,348 "
All other uses	157,400 "
	1,548,123 "

For fertilizers, acid of 50° to 60° Bé. is used both in the manufacture of phosphate fertilizers and in the manufacture of ammonium sulphate. Likewise for the pickling or cleaning from oxide scale, 60° acid is generally purchased although of late years the higher purity, together with the lower freight and cheapening of high strength acid, has led to the purchase of considerable contact acid for this purpose. For dyeing and electro-plating, as well as for the manufacture of many chemicals, the weaker acid may also be used. Acid of 66° Bé. is most largely consumed in the purification of petroleum, recovery of rubber, manufacture of explosives and in making mixed acid to be used for this purpose. For the making of mixed acid, however, the 98 per cent or oleum is being more largely used, since it permits the use of a weaker nitric and greatly decreases the cost of nitric acid manufacture without materially increasing the cost of the sulphuric. Spent acid (or mixed acid which has been used in nitration) is sometimes repurchased by the nitric acid manufacturer. It can, to a considerable extent, be used (with stronger sulphuric) for

the manufacture of nitric. Ninety-eight per cent (as well as 66°) is also used in purifying certain fats and greases, and fortifying weaker acid and weak nitrating mixtures in the manufacture of pyroxyline products. Oleum, or acid stronger than 100 per cent is used most largely in making mixed acid for the manufacture of explosives and using the entire output of the nitric plant, in making organic sulphonates and organic dyes, the manufacture of other chemicals and in fortifying or strengthening acid weakened by reduction so that the acid may be used again.

Cost of Manufacture. It is wise also to keep always in mind the intrinsic commercial values of materials. No mistake of the young engineer is more fatal to his success than the loss of the practical man's confidence incident upon a proposal to " kill flies with an 18-inch gun " as one of them expressed it.

The manufacturing cost (including interest on plant amortization, repairs, raw materials, labor, miscellaneous and " overhead charges ") varies in this country from about $5.50 per ton of tower acid (about 60°) to $9 for 98 per cent when made from waste smelter gases. As made from purchased ore for the chemical trade, costs vary from about $6.50 per ton of tower acid to between $9 and $12 per ton of H_2SO_4 in the form of 66° acid or 98 per cent.

Sales prices vary from $7.50 to $10 per ton of tower acid and from $12 to $20 per ton H_2SO_4 for high strengths according to quality, kind of package, size of shipment or contract, freight allowance, etc., " what the traffic will bear." These prices are generally quoted per 100 lbs., 1/20 of a ton, so quotations on " 66 o.v. " for instance will be upward of 60 cents.

Properties. The strong acid is a heavy, oily liquid, practically colorless, odorless when pure, but generally smelling strongly of SO_2 generally present in excess when the acid was formed. Its density approaches 1.9 times that of water at 15° C., the weak acid boils with evolution of water and the concentrated acid finally boils at a temperature of about 290° C. with decomposition into water, SO_2, SO_3 and oxygen. The strong acid has a heat capacity about one-third that of water and freezes in the neighborhood of 10° C. Strong acid and oleum have a powerful dehydrating action, breaking down the skin and many organic materials by robbing them of water and in some cases carbonizing and blackening them. Severe burns produced by sulphuric are best treated by the instant application of large quantities of water. Unless large quantities are available the acid should first be wiped away with something dry before washing, as the heat of dilution with small quantities of water or with alkali accentuates the burn. Quick removal of the acid, washing with water and after treatment with an emulsion of sterilized sweet-oil and lime water or ammonium carbonate makes a satisfactory treatment. For the eyes bicarbonate of soda should be used instead of the stronger alkali.

Corrosive Properties. Sulphuric acid with commercial impurities attacks practically all metals including platinum. The attack on platinum, however, is ordinarily very slow. On iron it is slow for acid exceeding 65 per cent, on lead for acid less than 65 per cent. Heat increases the rate of corrosion in all cases unless the boiling point of concentrated acid is exceeded. Gaseous acid, water, SO_2, and small quanities of SO_3 do not strongly affect either lead or iron but condensation must be avoided or the strength of the condensate, if any, carefully considered. Liquid or dissolved SO_3, however, has a peculiar action on cast iron, appearing to enter the pores and disrupt the casting, sometimes with a violence approaching explosion. Steel, semi-steel and to some extent malleable iron castings may be used as substitutes in this case. Corrosion by the liquid acid of wrought iron pipe is much less than that of steel, but it is to be remembered that nearly all pipe sold as wrought iron is really steel pipe. The great hydroscopic action of sulphuric is an important factor in corrosion of vessels and pipes. If air be allowed free access to the pipes the acid rapidly dilutes itself by absorption of moisture from the air and corrosion proceeds quickly. Where iron and steel are concerned, therefore the air should either be dry, or as far as possible excluded.

One fact should always be remembered; corrosion of metal goes on to some extent under nearly all conditions, more or less hydrogen is produced and it is extremely dangerous to use an exposed flame or a worn electric wire near such vessels without insuring the absence of " knallgas." Washing out with water should be avoided as much as possible and done only after previous emptying and cleaning from mud. Then an excess of commercial hydrated lime, powdered quicklime or even air-slacked lime or soda ash may be used but certainly a powerful stream of water should be intermittently supplied and the vessel allowed to empty itself completely at frequent intervals until the water is neutral. In sending workmen into such vessels the possibility of asphyxiation should always be guarded against.

Sources of Raw Material. Three principal sources of sulphuric acid are, native sulphur, sulphide ores and those gases which were formerly wasted in technical work, from smelters, etc.

Sulphur. Crude sulphur for making sulphuric acid comes from two principal sources, volcanic deposits of Sicily and underground beds in Louisiana. Russian, Caucasian, West Indian and Mexican deposits are also being developed. It occurs chiefly mixed with limestone, supposed to have been produced with the sulphur by the reducing action of carbonaceous matter and heat on calcium sulphate. There are numerous scarcely developed deposits of this nature in the United States.

In Sicily sulphur is mined on the south from Cataisia to Girgeute. It is separated from the gangue by fusion and distillation [1] and comes into the American market as dirty yellow lumps of irregular shape and

[1] See "Mineral Industry," Vol. VIII, p. 592.

size. The Louisiana deposits are attacked in a peculiar and ingenious way by (Frasch [1]) boring and piping the hole, forcing down high pressure steam to melt the sulphur deposit around the end of the pipe and then supplying air to raise the mixed column of water, air and sulphur to the surface.[2] The sulphur thus obtained is of a better quality than much of the imported article.

A fair idea of the purity of crude sulphur may be given by the following analysis of a product worth about $18 to $20 per ton. S = 95.4, Ca, Sr. Mg. all figured (as Ca) 1.5, $SiO_2 = 1.3$. The Louisiana sulphur is 99.6 per cent pure and sells for about $22.

Pyrites. Pyrites, FeS_2, carrying often more or less CuS is, at present, by far the largest source of sulphur for acid making. Its use began about 1830.[3] Considerable quantities are imported, chiefly from Spain,[4] Portugal and Newfoundland.

Deposits in the United States have been developed in New York, New Jersey and several of the southern Appalachian and far Western States. Most of them are not as high grade as the imported ore, but some are of the finest character.[5] Copper, zinc, calcium, magnesium and sometimes lead are objectionable from the point of view of the acid maker, as they retain sulphur that oxidizes to sulphate and is not available for burning. The lead and zinc otherwise interfere, by volatilizing. For roasting to produce SO_2 the per cent Cu $\times .505 +$ per cent Ca $\times .799 +$ per cent Mg. $\times 1.31 + 0.6$ (const.) may safely be deducted from the analytical per cent of sulphur in the ore to ascertain the probable actual sulphur value. But this is by no means all, as it is not proper to value ore directly in proportion to the amount of sulphur available. Allowances must be made for the increased cost of handling the gangue both as

[1] U. S. Patents 461,429, 461,430 and 461,431 of 1891.

[2] See *Eng. and Mng. Jour.*, Dec. 14, '07. Day Allen Willey, p. 1107.

[3] Lunge, "Sulphuric Acid and Alkali," third edition, Vol. I, p. 36.

[4] Analysis of some Spanish ores with cost at works 100 to 300 miles from seaboard are given for comparison per 100 lbs. of sulphur contained in the ore.

	S.	As.	Cu.	Fe.	Pb.	Zn.	Gangue.	Price
Roi Tinto lump	49.69	.72	3.12	44.01	.86	.38	.....	.82
Rio Tinto lump	47.95	....	....	....	....	....	.....	.55
San Tolmo	49.9	.11	1.7	43.8	....	....	6.2	.59
Zalamea	49.4	.39	.46	46.21	.47	.12	.....	....
Peruna	45.	....	....	....	....	....	.....	.81

Prices are generally made "per unit" which means per ton per per cent of sulphur. Peruna, therefore, at 81 cents per 100 lbs. of sulphur would be $16.20 per short ton of sulphur. This means $7.29 per ton of ore. If $1 freight had been paid, this makes the selling price $6.29 per short ton of ore which would be quoted at $6.29 ÷ 45 = 13.9 cents per unit (short ton.)

[5] Numerous analyses of United States ores are given in Lunge, "Sulphuric Acid and Alkali," third edition, pp. 57, et seq.

ore and as cinder and for the larger installation and repairs required where low grade material is used. Also the losses in cinder are absolutely larger with low grade ores but even the same loss (say 2 per cent) is equal to 4 per cent of the total sulphur in a 50 per cent ore, 5 per cent of the total sulphur in a 40 per cent ore.

Waste Gases. The third source of sulphur is waste gases, particularly the "fumes" from sulphide smelters. Copper is present in great quantities of Spanish ore that is imported for its copper value as well as for the sulphur, and the first step in the wet copper process is to burn out the excess of sulphur from which acid is made. In smelting zinc and copper ores a quantity of SO_2 is produced which is also turned into acid. These gases are otherwise at present worthless and are in many places a source of great expense to the producers owing to damage suits by those whose crops or trees are injured thereby. This damage is denied, but the fact remains that the vicinity of a sulphide smelter is desolated. This source of sulphur for acid production promises to exceed all others.[1]

Sulphur Burning. In burning sulphur three points chiefly have to be considered, i.e., freedom of the gases from volatilized sulphur which has not been oxidized, sufficient richness of the gases for profitable operation of the sulphuric-acid making portions of the plant, and as complete removal as possible of sulphur from the slight residue of mineral matter. It is a familiar fact in domestic economy that sulphur used for sterilizing does not burn up completely. Provision must be made for maintaining a sufficiently high temperature of the surrounding walls and of the material on which the sulphur is supported. For the latter purpose an iron plate is generally used, cast iron preferred, and it should be heavy enough and hot enough to insure active combustion of the sulphur at all points, even where the collected mineral residue is practically all that is left and only a small percentage of sulphur is being burned out of it. For this purpose special ovens are constructed. Provision is generally made for the preliminary heating of the iron pans and when once lighted the burners should either be operated in battery or fed continuously, so that

[1] Careful study of the question for years leads me to believe that (in practically all cases) it is feasible to recover such fumes, that marketable products can be profitably produced in any locality where large smelters now operate, that the value thus produced will in many instances exceed that of the metal produced and that no other phase of the sulphuric acid industry is so important. A single company at two plants is at present wasting enough sulphur to nearly equal the sulphuric production of the United States and defends damage suits and injunctions in preference to developing the probable outlets for chemicals it might produce. Zinc smelters located in the Eastern and Central States have already profited largely by the use of this former waste. Two copper companies in the South have done something in the same direction, producing 450 to 500 tons a day where they will ultimately produce several times this amount, but when there is no ready sale for acid as such, "policy"(?) prevents the development of methods for utilizing these sources of sulphur. The smelter gases vary considerably in strength of SO_2, contain much dust and metallic oxides, sometimes precious metals, as well as considerable quantities of carbon dioxide and some carbon monoxide.

the variations of operation of the single burner shall not directly affect the strength of the gases to any material extent. The necessity for accurate draft regulation is apparent. Too much draft is better than too little

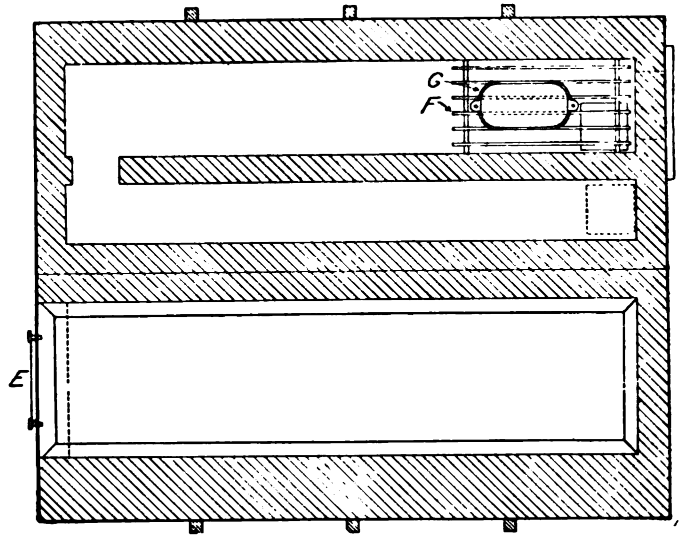

FIG. 110.

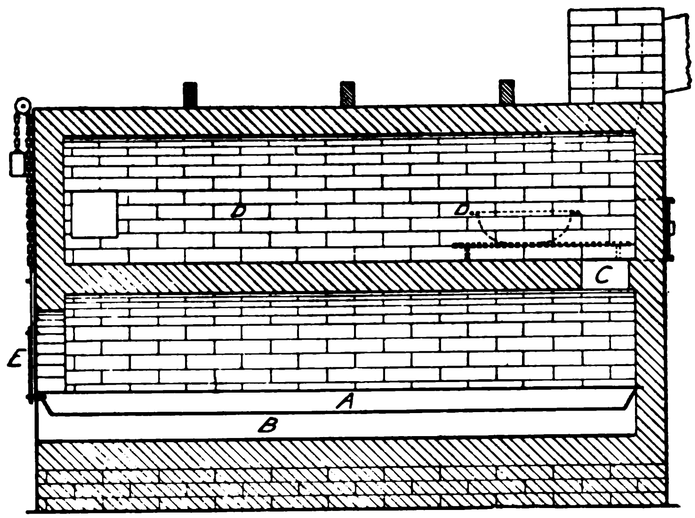

FIG. 111.

if ample provision has been made for the complete interaction of the gases before they are allowed to cool. In some types of burners in which the gases are drawn away too quickly from the burning pan an excessive supply of air serves to chill the vapors and promote the deposition of

sulphur in the flues. The indication of such action may be found in cloudiness of the Glover acid or filming with sublimed sulphur in the chambers. Figs. 110–111 illustrate onet ype of furnace recommended. The burner consists essentially of a shell of brick work having an upper and lower chamber, the division between the two acting as a reverberatory over the pan *A* in which the sulphur is burned. Draft is regulated at the door *E*. The fire is cooled when necessary to retard the vaporization

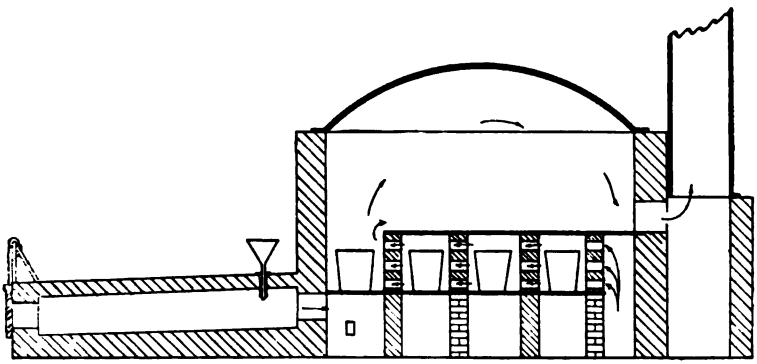

FIG. 112.

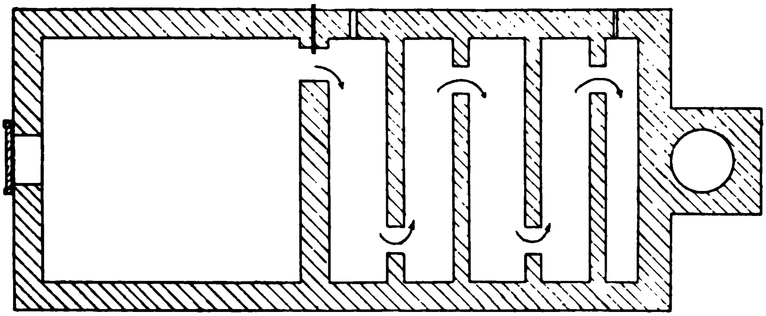

FIG. 113.

of the sulphur by means of admitting the air to space *B* beneath the plate. Products of combustion pass up through the hole *C* into the upper chamber *D* where opportunity is given for the interaction of sulphur vapor with the excess of air. A division wall in this upper chamber insures longer passage of the gases before cooling. A small hole above the inlet opening *C* into this upper chamber admits more air if necessary for the complete combustion of the sulphur vapor. Iron supports *F* are provided for a niter pot *G* when it is preferred to furnish niter for the chambers in this manner. This is one of the intermittent type of burn-

ers, generally operated in batteries. The exact regulation of draft is very difficult and extreme care in periodic rotation of charges is essential to successful operation.

Many burners have been designed and a number successfully operated on the continuous plan. One of the earliest of these [1] is illustrated by Figs. 112–113, and taken from Lunge's "Sulphuric Acid and Alkali," pp. 57 and 58. While not strictly continuous it would be necessary to open the door of such a burner only on rare occasions to remove cinder.

Burning of Pyrites. Like coal, pyrites ore was not recognized as a combustible until early in the last century, various claims dating from 1793 to 1820. Probably the necessity of desulphurizing cuprous pyrites in the works of Perret et Fils and the exhaustive work done by them is mainly responsible for its success. The heat of combustion must be conserved and therefore considerable masses are required to maintain the fire. As with coal, a certain weight (two to three pounds) can be burned per square foot of grate per hour, the depth of fuel bed (on top of cinder) generally varying from 10 to 30 ins. Excessive charges lead to loss of sulphur in the cinder, excessive depth of fuel to improper composition of gases and scarring or fluxing which corresponds to the formation of clinker in an ordinary coal fire.

The first step in the burning of pyrites is to properly adapt the size of the ore to the character of burner being used. Although ore may be purchased on contract relatively free of fines or small ore, it is generally desirable to render the plant as independent as possible of market conditions. Added crushing machinery for reducing all ores to fines and burning it all in this condition, may even be preferred. The cost of crushing and grinding in a well designed plant is small, the labor of crushing is less than the increased labor of operating lump burners, and furthermore the cinder from fines ore is always better burned and the waste of sulphur in this way is always smaller with the same composition of ore. Properly operated they are without question more economical, but they present certain drawbacks which should be recognized.

First, the greater amount of dust produced and in consequence thereof the greater volume of the dust chambers.

Second, the greater cost of repairs for most types of the burners themselves, as they require more or less frequent renewal of rakes or rabble blades, and at long intervals some of them require a complete renewal of all arches. The crushing machinery also requires continued repairs and many manufacturers prefer not to thus involve themselves. It is, however, generally possible to obtain a sufficient quantity of fines for regular delivery at attractive prices.

[1] Another type used in Brussels, Belgium, prior to 1882, employs the heat from the sulphur burning in the arched cast-iron shell to melt sulphur in a chamber. This molten sulphur is allowed to overflow through nozzles and fall upon the base plate burning as it falls and completing its combustion on the plate.

Crushing Ore. If run of mine ore is purchased, lumps may exceed 12 or 14 in. diameter and a heavy crusher of the general Blake pattern, illustrated[1] in Fig. 114, should be provided and located preferably below the ground level. Feeding should be done from an iron sheathed plank or cement floor. If lump ore is to be burned the product of the breaker should be elevated to a rotary screen of punched metal plates of $\frac{1}{4}$ to $\frac{3}{8}$ in. in thickness the holes in which being $\frac{5}{8}$ in. in diameter. The amount of fines made will be dependent upon the diameter of these holes, the character of the ore and the speed of the crusher. Five-eighths inch holes with a crusher running approximately 100 R.P.M. will produce from 12 to 30 per cent of fines. From the rotary screen, or riddle, the

FIG. 114.—Pyrites Crushing Rolls.[1]

fines should be allowed to fall into a small hopper, and the lumps into a larger one. If all ore is to be burned as fines there should be placed, preferably below the breaker, one or better two sets of rolls illustrated[1] in Fig. 115, and the breaker should be set somewhat closer. The breaker may then be expected to reduce the ore to about $1\frac{1}{2}$ to 2 in., the first rolls to 1 in. and the second rolls from 1 to $\frac{3}{8}$ in. or less. For the delivery of fines ore to fines burners a belt conveyor is well adapted and Link-belt carrier conveyor with tripper has been used.

Weighing the Charge. For lump burners the charges are required to be weighed with moderate accuracy, this is best done by drawing directly from the hopper into the small industrial car standing upon scales specially introduced into the track for that purpose The charge for each burner is thus separately weighed and dumped before the burner.

[1] Made by G. V. Cresson Co., New York City or Philadelphia.

Lump Burners. The lump burner is nothing more than the simplest pattern of deep-bed coal fireplace. As, however, the value of its work is dependent on the production of a rich and reliable gas, too much care cannot be given to its exterior tightness, the ability to regulate drafts accurately, and to shake out the cinder evenly. Also, as it is designed to produce hot gases for concentrating acid, the loss by radiation from both burners and flues should be as small as possible. In the long run constructive economy at this point is apt to be false economy. The money spent in thoroughly encasing the burners and properly insulating them will pay large interest.

Fig. 116 shows a good type of burner in which the common flue is provided with a double arch top. All doors are either hinged or their faces

FIG. 115.—Pyrites Breaker.

inclined, carefully planed, and therefore swing by gravity or latch against the planed edges of the door jam, allowing little leakage. The ash pit door D is perforated with 7 or more 1-in. holes, which can be plugged to regulate the admission of air below the grates. This arrangement is found more satisfactory than a wheel or slide damper because the adjustment is less likely to be displaced by accident. The doors E admit the shaker to the grate bars and also permit, to some extent, barring near the grate level. The doors C are likewise provided for the latter purpose, raising large scars to the surface of the bed, but are ordinarily not often required and may be made of the slide pattern and puttied tight if desired. Through the door B the charges are introduced, and distributed as quickly as possible over surface of the fire bed. The upper doors F, also slide doors, are not open except for occasionally cleaning the upper flue and may therefore be puttied up between times. The cross-section

of the upper flue should be carefully figured to avoid rapid currents of gas that would interfere with the exit of gases from the individual burner. These burners are generally built from 4 to 5½ ft. wide and 4 to 6 ft. from front to back.

Niter Potting. Fig. 116 also shows one method of potting niter (for supplying the nitric oxides to the chambers). The nitrate of soda and

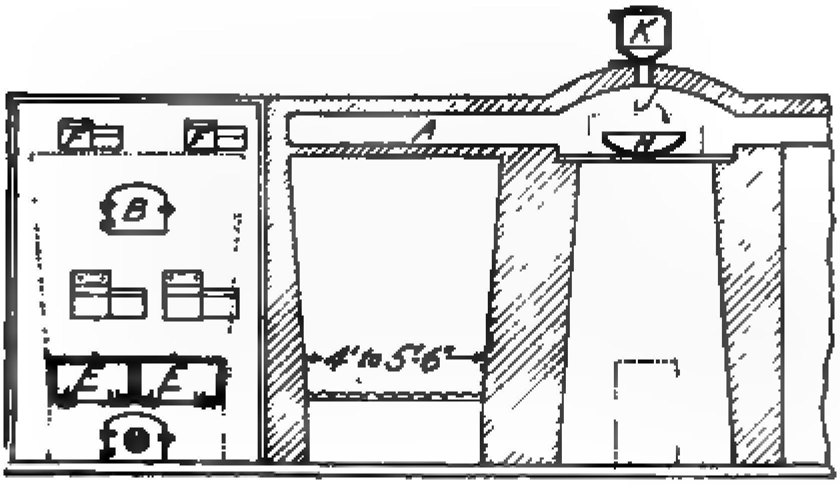

FIG. 116.

sulphuric acid are charged through a tightly covered hopper K, into the cast iron vessel H, which is supported on a plate in an enlargement of the common flue. Being thus subjected to heat from the burner the nitric acid is distilled out. The door J, is provided for removing the entire vessel. The vessel may also be provided with a spout and a greater excess of sulphuric acid used so that the mixture remains fluid while hot and can thus be run out when a temporary clay plug is removed. If niter is to be potted in this manner it is best to provide a number of pots operated in rotation and at short intervals, but the most satisfactory way of supplying niter to the chambers is generally in the form of weak nitric acid. The manufacturer of sulphuric acid located where no nitric acid is made, cannot generally buy at satisfactory prices or afford to pay the freight on it for this purpose and is therefore reduced to the potting of niter.

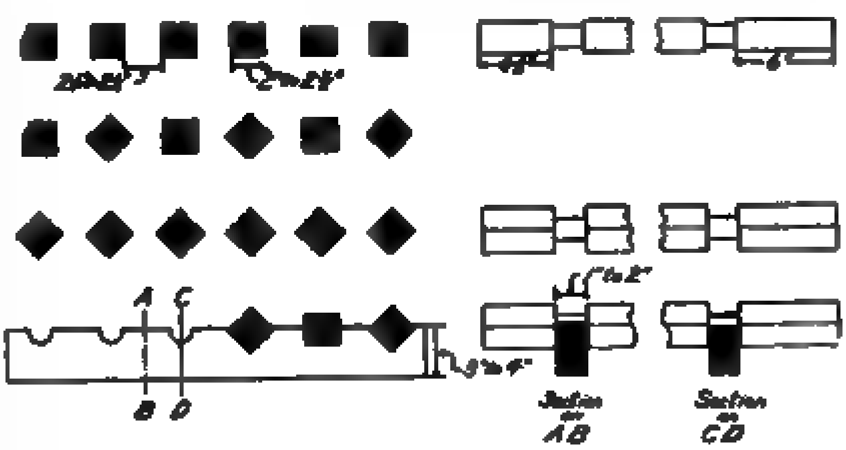

FIG. 117.

Grate Bars. Grate bars, detailed in Fig. 117, may be made of either cast or wrought iron, the latter being more expensive, but in many instances more satisfactory.

Shaking. Shaking is done by a crank handle shaker, which is sometimes provided with two handles equidistant on opposite sides of the

center rod so that both hands may be used or two men may operate the shaker. Alternate bars across the burner are generally shaken and the intermediate bars at the next period with such additional treatment as is required to evenly bring down the cinder. This cinder is generally allowed to accumulate in the ash pit and is removed once in twenty-four hours with a view to reducing the amount of air allowed to leak into the burners. From 500 to 900 pounds can be handled in each burner in twenty-four hours dependent on the quality and richness of the ore. Both for economy of construction and saving of heat, burners are generally built in double lines back to back; it is surprising what a difference in operating two or more such double lines can be noted between the operation of those burners which face one another and the burners on the outside facing the walls of the building. Good insulating burner walls are important—second only to stability of construction.

Operation of Lump Burners. The burning of pyrites

$$2FeS+5\tfrac{1}{2}O_2=Fe_2O_3+2SO_2+2O_2 \text{ [1]}$$

well illustrates a type of combustion which is extremely easy when draft is properly regulated and sufficient mass of the material is involved, but which was for many years regarded as impractical because the exact conditions required were misunderstood. Unlike coal, practically all pyrite is fusible. Too active a combustion, i.e., too free a supply of air in a large fuel bed produces too high a temperature (about 900°), causing the pyrites to melt and "scar" or clinker, cementing the unburned lumps together, sometimes enclosing them entirely, thus rendering it practically impossible to burn them until broken up, and impossible to pass them through the grates. A precisely similar result attends insufficient draft in certain localities of the burner, particularly in burners of large size. In this case the high temperature results not from too rapid combustion but from too small an excess of air to carry away the products of combustion as well as the excess of heat at surrounding points. The temperature theoretically obtainable by combustion of pyrites exceeds 1000° C., which is considerably in excess of that required to flux any of the usual grades of pyrites. The entire secret of success in pyrites burning, lies in proper regulation of charge and draft to suit the other fixed conditions of design of burner and character of ore supplied. Fortunately one excellent guide is always available, the analysis of the gases produced by the burners. This analysis should, when everything is running properly, be made at least twice a day while,

[1] Numerous secondary reactions occur such as direct oxidation of FeS, CuS, ZnS, etc. to sulphates followed in the case of iron by decomposition into FeO and $2SO_3$, when the temperature reaches approximately 550° C. Similar reactions occur with copper but at a higher temperature. With zinc it is necessary to raise the temperature to a bright white heat. Hence the sulphates once formed in the burners cannot be decomposed without danger of melting the pyrites.

if difficulties are being incurred with the burners, it is well to make such analyses hourly. With so many variable factors to consider it will perhaps simplify matters (after making the setting tight) to fix the draft at such a point that the analysis of the gases shall lie between 5 and 8 per cent SO_2 and should the burners then be too hot, carry a shallow bed of fuel. This is secured when already operating by omitting or greatly reducing a few charges without proportionately decreasing the amount of cinder shaken down, until hot cinder appears, after which the amount of cinder shaken can be reduced to equality with the smaller charge. Both draft and charge should then be increased gradually until the capacity of the burner is obtained. Herein lies the value of being able to determine what percentage of sulphur may reasonably be expected as inevitable in the cinder from a given ore, and the necessity of daily or at least semi-weekly determination of sulphur in the cinder.

All work that it is necessary to do with the burners should be done as rapidly as possible so that doors may be open the minimum time. The successive rotation of the burners should be as regular as clock work. If the number of burners in a set (frequency of charging) is such that two burners are to be charged at once they should always be as nearly as possible diagonally opposed to each other on opposite sides of the set and the rotation should be so arranged that the period of greatest heat occurs in burners half the length of the burner set from each other. No red hot ore should ever come through the grate bars; in fact, working with any usual depth of fuel bed, the ore when shaken down should be fairly cool. Proper burning of the cinder is superficially indicated by lightness, porosity of surface and a clear red, brown, or black shade (according to the character of ore) with little evidence of mottling, streaking or apparent hard spots. When broken the ore should show no kernel, or hard center but should have substantially the same texture throughout, except right at the surface it is likely to be more porous and frequently is checked by numerous cracks.

Fines Burners. The early designs of narrow staggered shelf burners, and broad shelf burners rabbled by hand need hardly claim our attention to-day in view of the extent to which the mechanical furnace has been developed. McDougall Bros. started the development of the circular or rotary fines burner in the seventies in England at about the same time as Perret in France. Modifications were made and patented from time to time by these inventors, by Mackenzie, Frasch, Herreshoff and others. The two latest and most perfect rotary patterns are the air-cooled O'Brien and the water-cooled Wedge burners. Even though the former is almost a toy compared with the latter it fills its place in smaller works burning 5 to 15 tons a day. The best running capacity of the O'Brien on high grade ore smaller than ½ in. is about 6000 to 7000 lbs. per day. The same furnace can properly burn 9000 or even 10,000 lbs., but repairs become excessive. Wedge furnaces range from 12 to

32 ft. in diameter, with 5 to 7 hearths. The 21½ ft. furnace has a capacity of 28,000 to 48,000 lbs., and weighs about 304 tons.

The O'Brien Burner. Fig. 118 shows the O'Brien burner, the mechanical features of which need little explanation. The central shaft *A* is cooled by the vertical current of air passing up through it. The arms *B* are likewise hollow and subdivided lengthwise nearly to the outer end in such a manner that a portion of the current of air is drawn out sidewise through one side and back again to the hub by the draft of the central shaft acting as a stack. The arms are secured by hubs *C* tightly fitting into the central shaft. The inner end of the arm tapers, is inserted with the

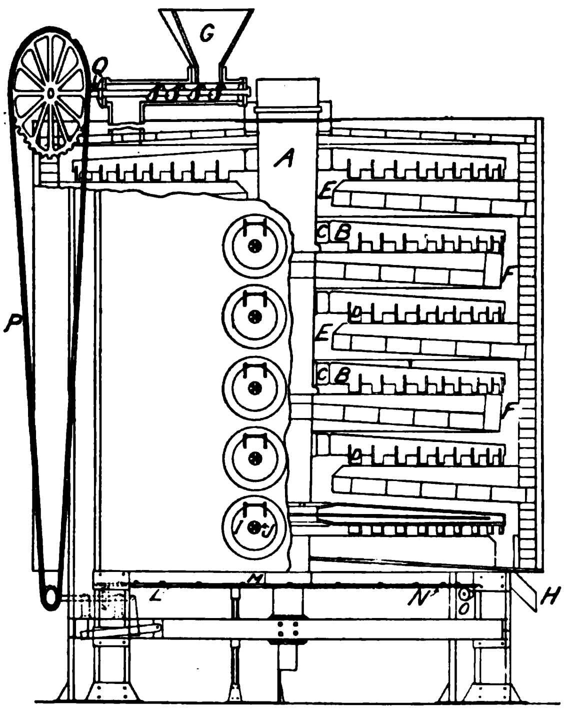

FIG. 118.

blades *D* turned sidewise and locks with a quarter turn on its own axis in the direction which the drag of the ore on the blades along its bottom tends to continue. Thus the action of rotation around the central shaft tends to lock the arms more firmly into the hubs, at the same time they can be turned up in the opposite direction by a special tool, removed and replaced in a few minutes. The rabble blades are cast as part of the arm, and given an angular position. They are carried around the central shaft, slowly moving the ore outward or inward on the alternate shelves. The shelves raked inward have an opening *E* around the central shaft through which the gas passes up and the ore falls down. The alternate

shelves have openings F at the periphery for the same purpose. A screw feed from the hopper G gives an excellently regulated supply of ore and the cinder passes out through the bottom chutes H that supply a portion of the air for burning. Two doors I are provided to each shelf for removal of arms and have wheeled draft openings J that serve also as peep-holes for observing temperatures. Access to these peep-holes and to the top of the burner is provided by iron-side ladders, and a movable working platform of wood serves when removing the rake arms. The hot air from the burner shell and the central shaft are profitably used in thoroughly drying the ore. Rotation is imparted to the shaft A by a very cheap and simple gear which is nearly the whole diameter of the burner and is made by bolting segmental sheets L of $\frac{3}{16}$ in. steel to a flange M on the lower end of the shaft, uniting the periphery of the circular plate thus formed with cheap cast iron sections of curved racks N which in turn rest upon small pinions O. If anything catches inside the burner the weight of the rack becomes insufficient to keep the gears meshed and the racks jump without breaking or injury, only making enough noise to call attention quickly to the trouble. A vertical chain drive P actuates the large sprocket on the screw shaft Q from the main pinion shaft below.

The Wedge Burner. The Wedge burner, Fig. 119, is naturally more substantial in every respect as required by its heavier duty. The central shaft A is large enough to admit a workman, its temperature being at all times low enough to permit his making any repairs that may be necessary. Each arm B is separately water-cooled and strongly secured to the shaft by a heavy breech block C, also water-cooled, while the rabble blades are individually removable and replaceable with practically no interruption of the furnace. The hearths are level and have openings E near the shaft and F at the outer edge for dropping ore and permitting the rise of gases. The entire top of the burner G serves as a combined feed hopper and feed table being provided with its own special arms and tripper rakes that swing back under the excessive load of deep piled ore thus regulating the feed at the center even if the ore is piled high at the sides, at the same time gradually distributing such a pile evenly. The supply of ore entering around the shaft through a sand-lute continually renews the lute and further regulates the feed, cinder being discharged through the chute H. Repair doors I, poke and peep-holes J are likewise provided. The central shaft, all arms and moving parts are supported on the gear M, by means of the four roller bearings N, traveling on the smooth outer face of the gear, the whole being merely centered by the bottom pin P giving a rigid central shaft with no "steppe" or base block, practically without wear, friction being almost wholly rolling. Obviously the feed is here strictly dependent on the operation of the rake arms and over feeding or clogging is almost impossible as is also the failure of the water-cooled arms. Nevertheless the driving pinion O is actuated by a

shear pin in the hub of the gear *O* that cuts off if any serious obstruction takes place in the furnace.

For the burning of special ore, zinc blend, etc. particular types of furnaces have been devised, but it is not within the province or space

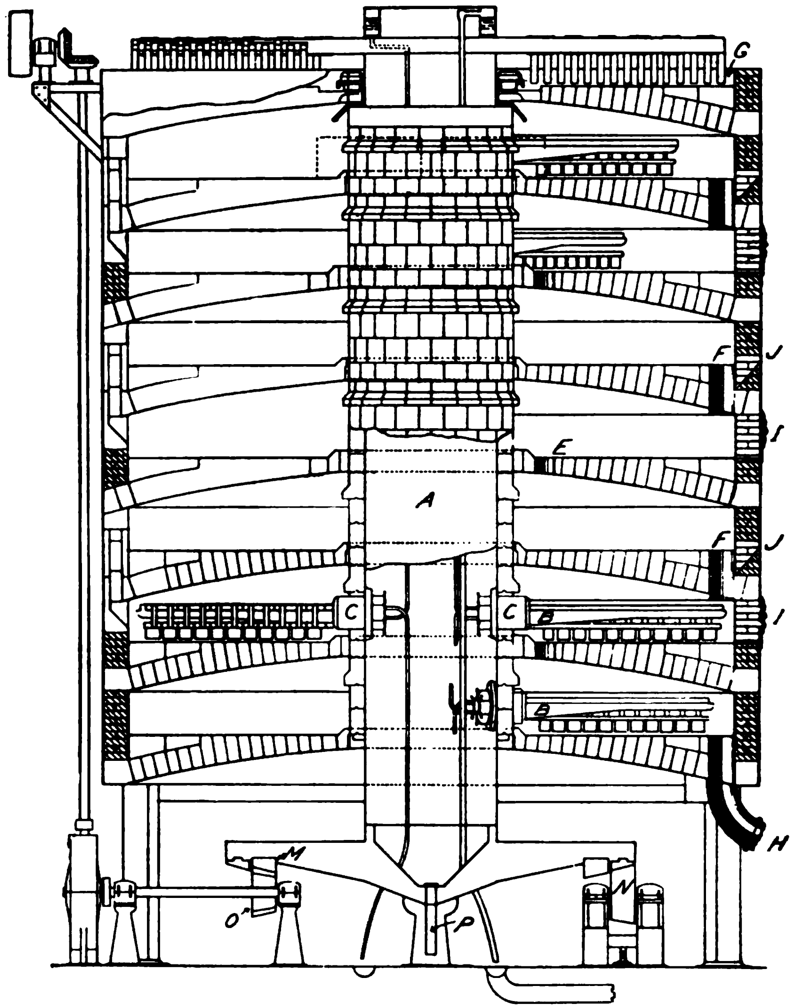

FIG. 119.

allotted for this work to consider them in detail.[1] Other types of fines burners are built on the drag conveyor principle or reciprocating rake principle, but are less used than the rotary furnace and less practical for most purposes.

[1] A number of devices for this purpose are indicated in Lunge's "Sulphuric Acid and Alkali," and in the special books on metallurgy.

Operation of Fines Burners. Mechanically the operation is extremely simple, consisting of feeding substantially equal quantities of ore in equal periods of time by means of a ram, screw, rake, or similar device. The regularity of the feed is of great importance so that conditions effecting it, i.e., speed of shafting, etc., should be properly controlled. Nearly all types of burners make the feeding device subsidiary to the rotating mechanism, stopping the feed in case for any reason the rotation ceases. This is most perfectly done in the Wedge furnace. The skipping of the O'Brien only calls attention to the trouble. While it is obviously necessary to prevent the clogging up of the burner, it is not by any means the only requirement. A 10 per cent variation in the speed of shafting either reduces the capacity of the burners or results in unconsumed sulphur. For most acid making purposes the air enters cold partly through adjustable openings in the doors and partly through draft openings in the bottom, gases increase both in richness and temperature in passing up through the burners, taking a long alternating course from the center to the periphery and back again for each pair of shelves. The rotating mechanism carries the stirrers, scrapers, shoes, ploughs or rakes as they are variously called, set at an angle alternately pointing inward and outward so that while the general movement of the ore is circular on each shelf, it is also spiral toward or away from the center. Also it is turned or rolled upon itself in such a manner as to expose all portions of the ore and being finely divided the best possible access of oxygen to the unconsumed sulphur is permitted.

Starting the Furnace. Starting of the furnaces is carried out in much the same way with lump or fines burners. When new they should be dried out slowly with small wood fires and a good supply of air, but with no violent draft. This requires from two to four weeks. The fires are then rebuilt on a cinder bed and forced steadily until the burner becomes red hot. The burner is then quickly cleared of large pieces of wood and the supply of ore started. Suspension of operation or hold-overs cannot be much prolonged with the smaller burners unless special precaution has been taken to jacket them against heat losses and provide most carefully against the leakage through doors. If this is done the fines burners hold over quite satisfactorily from two to five days according to size; lump burners hold over longer. Minor repairs to the burners require no hold-over, but should repairs to an arch be necessary, it is apt to necessitate a complete shut-down and over-hauling of the burner for which no period of hold-over would suffice and for which any considerable heat in the burner would make working impossible. The special tools furnished each type of burner require no particular description as their uses will be specific to the type of burner and almost obvious from their mechanical construction.

Regulation of Furnaces. Certain general instructions may be given for regulation of fines burners. The distribution of temperatures from

shelf to shelf is regulated by increasing the draft to raise the heat zone or by decreasing the charge when the lower shelf becomes too hot with the central hot zone too low. Sulphiding of rabble blades indicates too little draft or too rapid charging. The O'Brien burners are apt to show slightly decreased capacity in hot (summer) weather, less noticeable in the larger burners. Wedge burners can be operated on pretty wet (almost sloppy) ore but the O'Brien burners do not give their capacity unless ore is fairly dry—the drier the better. Very wet ore affects the Wedge capacity somewhat, but very much less because of the large hopper area of the top and the drying action that takes place there. One great advantage presented by the large burners with their enormously long travel of ore is the conversion of SO_2 to SO_3 by the partly burned ore itself. As much as 10 to 15 per cent of the SO_2 may be so converted with a consequent increase of chamber capacity and greatly improved action of the Glover tower.

Dust Prevention and Collection. As has been stated the use of fines burners is advantageous in most respects. Proper design and selection can overcome all serious objection to repairs. But the quantities of dust usually carried over into the Glover are objectionable. Little attention has hitherto been given to its prevention, but much to its collection. Without considerable expense for operating fans, *complete* purification of hot burner gases from dust may as yet be regarded as practically impossible.

Fig. 120.

Water-cooled Flues. Of the older styles of dust separators, Fig. 120 shows a water-cooled flue, in which the velocity and temperature of the gases were reduced, thus depositing the dust. In these enlargements the gases were supposed to come nearly to rest and lose the velocity which enabled them to carry the particles of dust along. They were found to be only moderately successful.

Baffle Plate Separators. Baffle walls or plates were then introduced, Fig. 121, and found to give much better results on very fine dust. Unfortunately their introduction subdivided the settling space and increased the velocity of the gas currents again. Numerous vertical partitions or curtains parallel to the direction of the gases, Fig. 122, with dampers for alternately shutting off one side while cleaning, also gave

good results, but were by no means satisfactory. The material had to settle too far and vertical currents circulated within the divisions owing to differences of temperature of the sides or top and the bottom.

Centrifugal Separators. A. P. O'Brien (Mineral Industry, Vol. 9, p. 632) introduced a centrifugal dust separator, Fig. 123, entirely feasible wherever a fan is used and giving excellent results for all larger sized dust. He adapted it to serve also as a niter oven, by introducing through the conical body *A* cast iron pots *B* that were hardly calculated, however, to improve the centrifugal action. The pots can be conveniently charged from the top and emptied from the bottom. Dust is discharged from the apex of the conical bottom without interrupting the operation. Only about 75 per cent of the dust from fines burners was recovered.

FIG. 121.

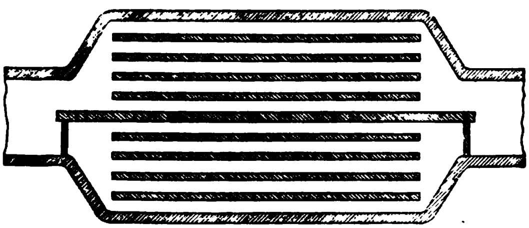

FIG. 122.

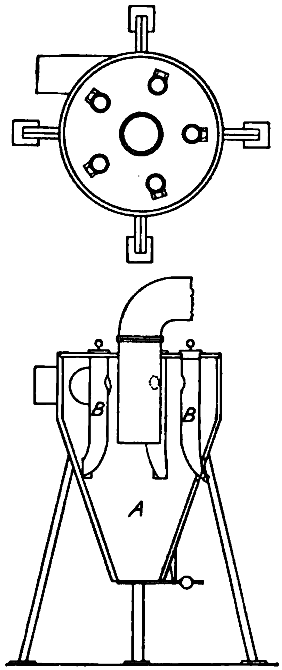

FIG. 123.

Modern Separators. Early in the efforts to purify gases for the contact system it was observed by workers here and in Europe that burner gas drawn through a 1-in. pipe into the laboratory showed practically no contamination of the contact mass. As will be seen later, this means a degree of purity which is almost absolute freedom from suspended matter. This peculiar method of purifying gases by slow flow through pipes of small diameter was pointed out by Knietsch in 1900 in his account of the preliminary work of the Badische Analin u. Soda Fabrik. Seeking, however, to avoid the multiplicity of small pipes that would be required by this method, Henry Howard, U. S. Patents Nos. 970,053 and 896,111 provides what has proven to be one of the best dust collectors yet devised. It consists of a series of horizontal parallel shelves, an inch or so apart across which the gases pass in a slow stream,

from a general inlet chamber to a general outlet chamber. The results obtained are truly astonishing, even dust ordinarily regarded as impalpable being largely retained. No attempt has been made in the patent to cover the process of purification by passage through small tubes and it is doubtful if this process would be patentable in view of the publication of Knietsch's results ten years ago. Some results obtained on a small scale indicate that the tubular form is an even more efficient purifier than the shelf, although of course the space occupied in the plant is not so efficiently used. Nevertheless it is apparent that a highly efficient dust collector could be so constructed.

Likewise in contact process work it was observed that gases could be purified to a surprising degree by "filtration" through layers of small coke lumps, cinder from the burners, etc. Dust catchers which consisted in filtering the gases through cinder were at first quite unsatisfactory, because the cinder used was itself a great source of dust and no provision was made for interrupting or alternating the gas currents while shaking out the lower layers that became clogged with dust. The inventor of the Wedge burner has, however, met these objections and given us a dust collector free from these criticisms. On inclined grates are supported sets of filters consisting of beds of marbles ½ in. in diameter and from 2 to 4 ft. deep. These make an extremely complete dust separation, much more so than irregularly shaped lumps and carry the collected material down with them.

Chamber Plant. The clearest understanding of the chamber plant will be obtained by first describing the general method of carrying out the process and then indicating modifications at one point or another with the changes in form of apparatus involved.

The sulphur gases obtained are constituted as follows:[1]

	SO_2	O_2	N_2	CO_2
Sulphur burners	11.0–6%	10.0–15%	79%	....
Pyrites burners	8.5–5%	10.5–14%	82%	....
Metallurgical gases	8.0–2%	10.0–6%	....	0–8%

The dust having been separated the hot gases enter at the bottom of the Glover tower (4), Fig. 124, and pass upward through packing or filling occupying the interior of this tower. Here they meet a downflowing stream of aqueous sulphuric acid, evaporate the water from this aqueous acid and give up part of their heat in the process, at the same time supplying a portion of the steam required for the first stages of the reaction in the chamber proper. Higher up in the Glover tower this moisture and heat perform a further function in that they help to drive out the lower oxides of nitrogen from the "nitrous vitriol" fed into the top of the Glover tower along with the aqueous acid.

[1] SO_3 varying from .2 to 2% is here included as SO_2 and G_2.

Near the top of the Glover is a favorite place for locating a fan (4) if none has preceded the Glover tower. At (4) the fan may blow horizontally, or vertically downward into the chambers.

It is customary to make the first chamber (5) fairly large, as the gases are at first converted rapidly. Removal of the end products by cooling and thorough mixing to facilitate further conversion becomes necessary. The addition of water in some form to take part in this further conversion does not arise until equilibrium is approached and the conversion begins to slow down. At this earlier stage in the process the corrosive action of the gases is greatest and it is not desirable to expose too great a surface to deterioration. The gases are generally, therefore, introduced into the large chamber (5) wherein approximately one third of the conversion is

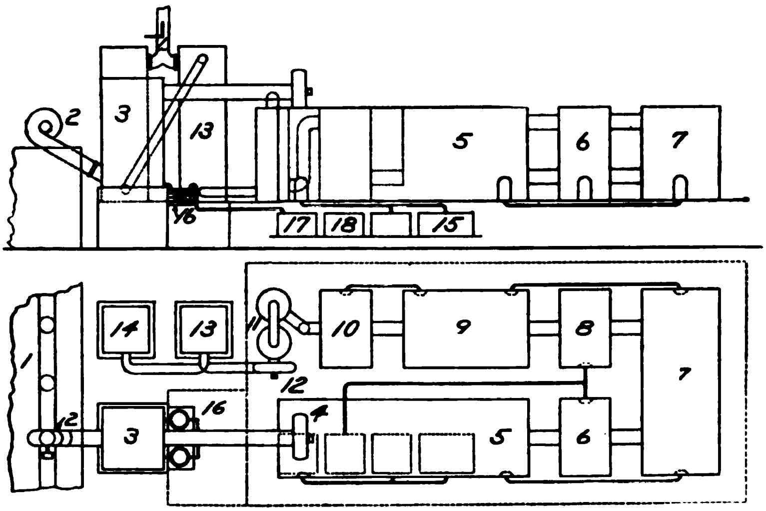

FIG. 124.

expected to take place. Some heat is removed by conduction and radiation from the walls and ceiling, condensation occurs on both these surfaces and to some extent incipient condensation in the mass of the gas owing to the formation of acid of a strength which is not volatile, which therefore tends to precipitate in mist or rain, so that in the later part of their passage through a large first chamber the gases require more moisture either as steam or spray. Personally the writer doubts the relative value of very large first chambers. From the first chamber in which approximately one third of the acid is usually produced (exception, see Falding, p. 185), the gases pass to other chambers or towers (6) to (10) which may be empty or may be provided with suitable packing or with perforated plates designed to promote the mixture of gases and moisten them by supplying acid or water at the top of the tower. The use of cold liquid sprayed into chambers or fed to intermediate towers (6), (8), (10) greatly increases the ability

to remove heat from the gases and makes up for the absence of conducting and radiating surfaces lacking in the larger sized chambers, or shut off by acid proof lining of the towers. Large empty chambers are more commonly used, or large chambers without packing, but alternated

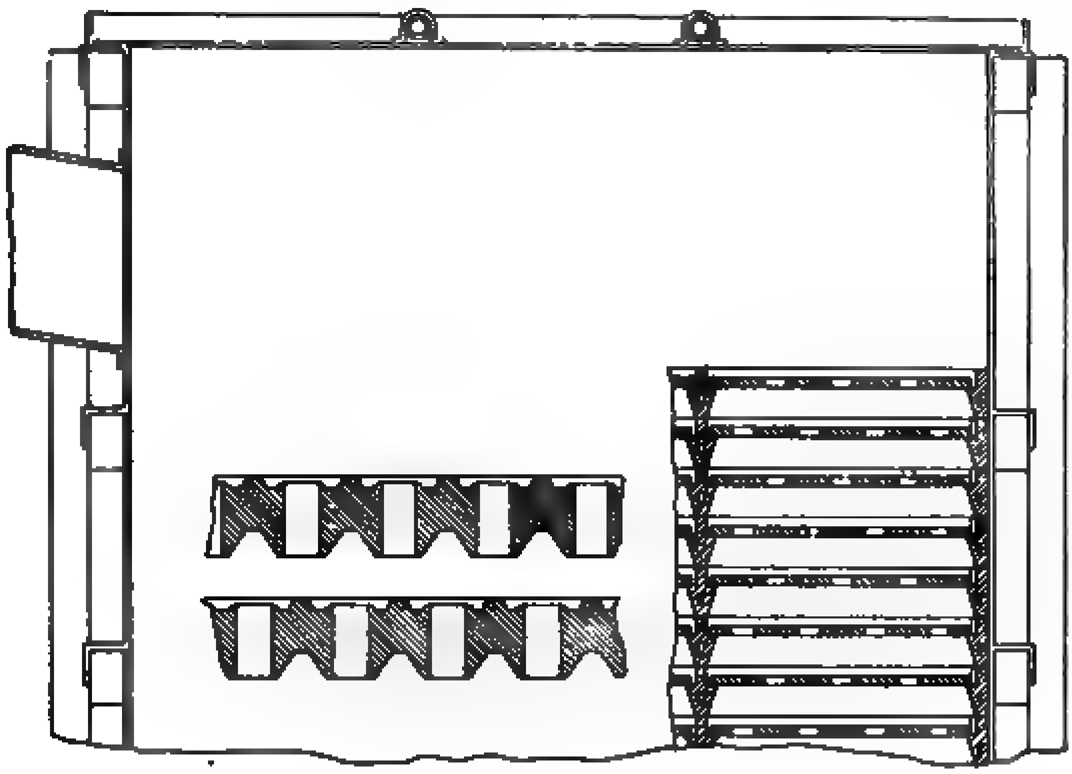

Fig. 125.

with high narrow chambers packed either with the Lunge-Rohrmann plates, see Fig. 125, or with some arrangement of bricks or tiles found to be cheaper. The purpose of any special arrangement is:

1. To promote the mixture of the gases.
2. To expose the largest possible surface of liquid to the gases.

3. To vary the temperature of the liquid surfaces as frequently and widely as possible.

4. To provide sufficient space (time) for practically completing the conversion of the SO_2 to H_2SO_4, under the conditions to which the particular design subjects it.

These chambers are followed by a cooling device consisting of either unpacked towers (11) or of a long flue connecting the chief reaction space with the apparatus for recovering the lower oxides of nitrogen after they have performed their function in uniting the SO_2, O, and H_2O to form H_2SO_4. Between the last chamber and the final (Gay-Lussac) towers is another preferred location for a fan (12) when used to furnish draft for the system. This absorbing apparatus[1] (Gay-Lussac tower) (13) is frequently duplicated by a second Gay-Lussac (14) to insure complete recovery by the lower oxides.

From the Gay-Lussac the gases now almost completely purified from both SO_2 and oxides of nitrogen are finally discarded through the stack. A fan is sometimes used here. If mechanical draft (a fan) has not been introduced somewhere along the line it is customary to introduce either a steam jet or a damper in the stack for regulation of draft. It is always best to provide both.

Having followed the passage of the gas, the equally important movement of the liquids should be considered. Sulphuric acid is formed in the last chamber by the bringing together of SO_2, O and H_2O by means of the oxides of nitrogen. It is precipitated upon the walls and collects on the floor of the chamber, being the weakest (48 to 50°) and purest acid made in the system. From here it is sometimes taken directly for separate concentration when a purer acid than ordinary chamber acid is required. Generally it flows forward into the next chamber where it is slightly strengthened by the stronger acid made in the warmer chamber, but it is also slightly contaminated by the greater quantity of dust settling there, the greater action on the lead walls and the greater amount of As_2O_3 etc. in the gas. And so on down the series of chambers until it reaches 52–54°. Thence it may be partly withdrawn for use and sale or for separate concentration, or taken to the storage tank (15). Most, if not all, of this acid may be elevated from the tank to the top of the Glover tower (3) and mixed with "nitrous vitriol" or run in through the sealed openings to mix with "nitrous vitriol" in the upper zone of the tower.

[1] Where one tower alone is used it is generally filled with coke, specially made acid-proof stoneware shapes, or pumice stone. Where two towers are provided the first is sometimes packed with Lunge-Rohrmann plates, Fig. 125, rhomboidal brick, or simpler open packing of stoneware, the second and final tower of the system with smaller rhomboidal brick, coke, or pumice. The Gay-Lussacs are supplied with strong sulphuric acid approximately 60° Bé. in which the lower oxides of nitrogen readily dissolve though not completely, always escaping to some slight extent with the exit gases so that one of the cost factors in the production of chamber acid is always the loss of "niter" which it is necessary to replace.

At first it is concentrated by mixing with the nitrous vitriol and then diluted from the steam condensed by the two cold acids. It also loses by conversion, anye xcess of oxides of nitrogen or SO_2 it contained and helps to liberate the lower oxides from their solution in the 60° "nitrous vitriol." Meeting the SO_2 of the burner gases the nitric and nitrosyl sulphuric are decomposed and the resulting oxides of nitrogen carried along by the burner gases. As it trickles down the acid is further heated by the hot gases and soon begins to lose water rapidly and becomes concentrated, flowing from the bottom of the tower into coolers (16) with strength of between 59 and 61° Bé. This is the "Glover tower acid" containing most of the arsenic and dust from the ore that is not held back by the dust catching devices (1). It generally contains a little SO_2 and is nearly free from oxides of nitrogen though quite capable of dissolving them readily when cold. A portion of this strong acid is elevated to the top of the Gay-Lussac tower (14) where it trickles down against the outgoing gases thus dissolving and recovering the final portions of the nitrous gases not absorbed in the preliminary Gay-Lussac (13). From the bottom of the Gay-Lussac tower the acid flows to a storage tank (18). The excess of this circulating acid formed by the continual addition of weaker nitrous vitriol from (14) is the strong nitrous vitriol that goes to the top of the Glover (3) and returns the recovered nitrous gases to the cycle of the process.

Reactions in the Glover Tower. The gases as they come from the burners usually contain from 6 to 8 per cent SO_2, 0.5 to 1.5 per cent SO_3, 8 to 12 per cent O_2, a little H_2O, some dust and nitrogen and are hot. With large dust chambers their temperature may be as low as 150 to 200° C. The hotter the better, however, for the work the Glover has to do. The reactions liberate much steam so that about half the moisture required for the chamber process is carried along with the lower oxides of nitrogen and SO_2 into the chamber. If the acid is diluted to about 58° Bé. (74.35 per cent) nearly all niter is liberated at which SO_2 greatly assists by acting on the niter itself. It is customary, therefore, to feed the top of the Glover with cold 60° (77.67 per cent) acid used at the end of the process (Gay-Lussac tower) for recovering the lower oxides of nitrogen, and also with water or chamber acid, preferably the latter, because the mixture can be more readily made outside the Glover with less heating and without evolution of nitrous fumes and because the chamber acid is thereby concentrated in the Glover instead of so much useless water being introduced into the system where it is not needed. This strong "nitrous vitriol" and the weak acid are often separately fed into the top of the Glover tower (3) through properly trapped holes (see p. 173), but are often mixed outside or just as they flow in. The cold acid condenses and absorbs steam rising from the lower part of the Glover and the packing of the tower should be of a character to facilitate their mixture and the heating of the liquid, but not to facilitate it too soon. The liberation of these

lower oxides in the Glover tower along with the moisture, gives us immediately the conditions requisite for the formation of sulphuric acid and, in a well operated and designed tower, there is accomplished here nearly 20 per cent of the total formation of acid of the chamber plant. To secure this and at the same time to secure freedom of the acid at the bottom of the tower from the oxides of nitrogen, several conditions are requisite.

First, the mixture of strong and weak acid should be equal and thorough.

Second, this mixture should penetrate to some degree below the top of the tower before being subjected·to too much heat.

Third, sufficient heat (120° F.) should then be applied to insure the rapid evolution of lower oxides of nitrogen in the presence of SO_2 and ample moisture before the liquid has penetrated too far down the tower. It is not rational, to use the same material for the entire filling of the Glover tower. Three distinct operations are to be carried out therein. At the top of the tower the nitrosyl sulphuric acid from the Gay-Lussac and weaker acid from the chambers is to be mixed together with any nitric acid that may be used for maintaining niter content of the system. Just below this mixing zone should occur the zone of heating and reaction, the reaction extending back up through the mixing zone and into the chambers. Next we have the zone of combined concentration and denitration in which the latter predominates. Up to a strength of approximately 59° Bé. sulphuric acid can be denitrated by hot sulphurous acid gas, but unless the acid is somewhat weaker, the reaction is not complete even in the presence of considerable water vapor from the concentration going on in the bottom of the tower. It is, therefore, desirable to have the acid reach the zone of final denitration not stronger than 58° Bé. The nitrogen compound most permanently resisting the separation from the sulphuric is the nitrosyl sulphuric acid. The dissolved gases are removed very much higher up. The reaction by which the last traces of nitrosyl sulphuric acid are removed is probably as follows:

$$2NO_2HOSO_2+SO_2+2H_2O=3H_2SO_4+2NO$$

This NO together with the remaining water from the concentration below proceeds on up the tower and is quite capable of reacting under the existing conditions for a further formation of the nitrosyl sulphuric acid, or of sulphuric acid direct. The oxidation of NO in the presence of sulphuric acid does not proceed to N_2O_4 or HNO_3. Probably the NO reacts with the sulphuric as follows: $2NO+2H_2SO_4+\frac{1}{2}O_2=2NO_2HOSO_2+H_2O$ though under the conditions at the lower portion of the zone this reaction would be slight. Likewise $2NO+2SO_2+H_2O+1\frac{1}{2}O_2=2NO_2HOSO_2$, a reaction more likely to occur at this point. Owing to the conditions of high temperature and ample humidity, however, neither reaction is likely

to proceed at all near completion and much NO will pass up the tower along with the oxygen and be converted into N_2O_3 by simultaneous absorption in sulphuric and oxidation.

Probably the reaction

$$N_2O_3+2H_2SO_4=2NO_2HOSO_2+H_2O,$$

takes place in the lower portion of this zone and the reaction

$$N_2O_3+2SO_2+H_2O+O_2=2NO_2HOSO_2,$$

somewhat higher up. The gases passing into the upper zone of the Glover tower carry an excess of moisture and are excellently equipped both by moisture and temperature to work the reversible reaction $N_2O_4+H_2SO_4=NO_2HOSO_2+HNO_3$. Here they likewise meet a liberal supply of nitrosylsulphuric acid brought from the Gay-Lussac towers mixed with the weaker chamber acid, which enables this reaction to be more easily reversed. The N_2O_4 resulting therefrom is in excellent position, therefore, to act upon any product in the upper portion of the tower immediately upon its entrance. The nitric acid added for the maintenance of the niter content of the system may well be the subject of this reaction for $HNO_3+3H_2SO_4+N_2O_2=3NO_2HOSO_2+2H_2O$. From the upper zone of the Glover tower, therefore, the gases pass off into the chambers at a temperature of about 60° to 90° C., generally under normal conditions about 80° C. with about 15 per cent of their SO_2 converted, laden with moisture and also laden with lower oxides of nitrogen.[1]

Below the mixing reacting and denitrating zones of the tower, begins the upper portion of the concentration zone. Here the gases contain so much SO_2 and are sufficiently hot and saturated with steam to eject from the down-flowing liquid all traces of nitrogen compounds, before reconcentration has progressed too far (58–59° Bé.), which would cause the acid to retain oxides of nitrogen. Finally at the bottom of the tower there should be sufficient zone of high temperature left for the concentration of all the acid to 60° Bé., preferably a little higher. To accomplish this, it is desirable to have a form of packing which shall not permit too ready down-flow of the liquid but shall retain it to some extent so as to delay its passage through the hot zone long enough to permit its ample

[1] In looking over the reactions which have occurred in the Glover tower it is not surprising that careful calculation indicates the oxides of nitrogen to have taken active part in one reaction or another approximately nine or ten times in a manner calculated to produce sulphuric acid. Therefore it is again not surprising that even in the relatively small space of the Glover tower, from 10 to 20 per cent of the total sulphuric acid "make" of the chambers is produced, an activity per cubic foot one hundred or two hundred times as great as in the chamber. Nor is it surprising that even distribution of the acid, both nitric and sulphuric, containing nitrous oxides must be maintained at the top of the Glover tower.

heating and concentration, while at the same time exposing sufficient surface of liquid to the hot gases to assist in the concentrating action. Herein lies the reason for conserving the heat by proper burner walls. This packing, however, should be sufficiently open in its structure to run no risk of becoming blocked up by the deposition of flue dust which has succeeded in passing the dust chambers. Ample dust recovery can be made by modern methods without reducing the gases below 400° C., since their usual temperature from lump burners ranges from 500° to 800° C. and from fines burners 450° to 600° C. It is generally safe to rely on gases being from 350° to 450° C., as they enter the Glover and some sets, even mixed fines and lump burners, exceed this figure.

Construction of the Glover Tower. The tower (Fig. 126) must, therefore, be constructed to withstand the severest duty. The almost universal practice is to make it of lead with joints constructed, as are the joints of the chambers etc. throughout the plant, by burning the lead together (autogenous soldering). For this purpose the lead (always first scraped clean where it is to be burned) is lapped, and a small oxyhydrogen or oxygasolene flame directed simultaneously against the edge of the outside sheet and a "strip" or stick of lead held in the other hand. The lead of the Glover is protected inside with the utmost care both from heat [1] and corrosion.

As the framework itself and the tower with its packing, top house and supply tanks at the top make a heavy load, a firm foundation of masonry becomes necessary. The foundation, or platform, should be well pitched, asphalted or preferably in the former case, covered with a thin layer of pitch and sulphur melted together. Then the whole top should be protected by the acid pan of 10-lb. lead. Wooden tower frames are very common and the sill may then serve as the edge against which the drip acid pan is turned up and over. Yellow pitch pine should be used and the sills and column feet may profitably be well pitched in setting, and dowel pinned.

There are two ways of joining the sheets for sides or curtains of a Glover tower, usually depending on whether the tower is square or circular. In the former case it is customary to suspend sheets from the top of the tower and make the joints vertical, avoiding the location of a joint close to a corner. In the latter case it is customary to make hoops or belts slightly smaller at the bottom and to lap each inside the one below. Square towers are sometimes made in this way. At the top of the tower the sides are bent over the strong frame which is intended ultimately to support the greater portion of the weight but the sides must also be secured to the diagonal bracing or horizontal cross

[1] Many designers attempt to cool the under side of the tower bottom by air channels, water circulating around the pan, etc., but even with the hottest towers of ordinary size this can be inexpensively avoided.

pieces of the tower frame by frequent straps to prevent their being sucked in or pressed out as the draft may act upon them and also to take a portion of their weight from the top of the frame. As a rule the sides

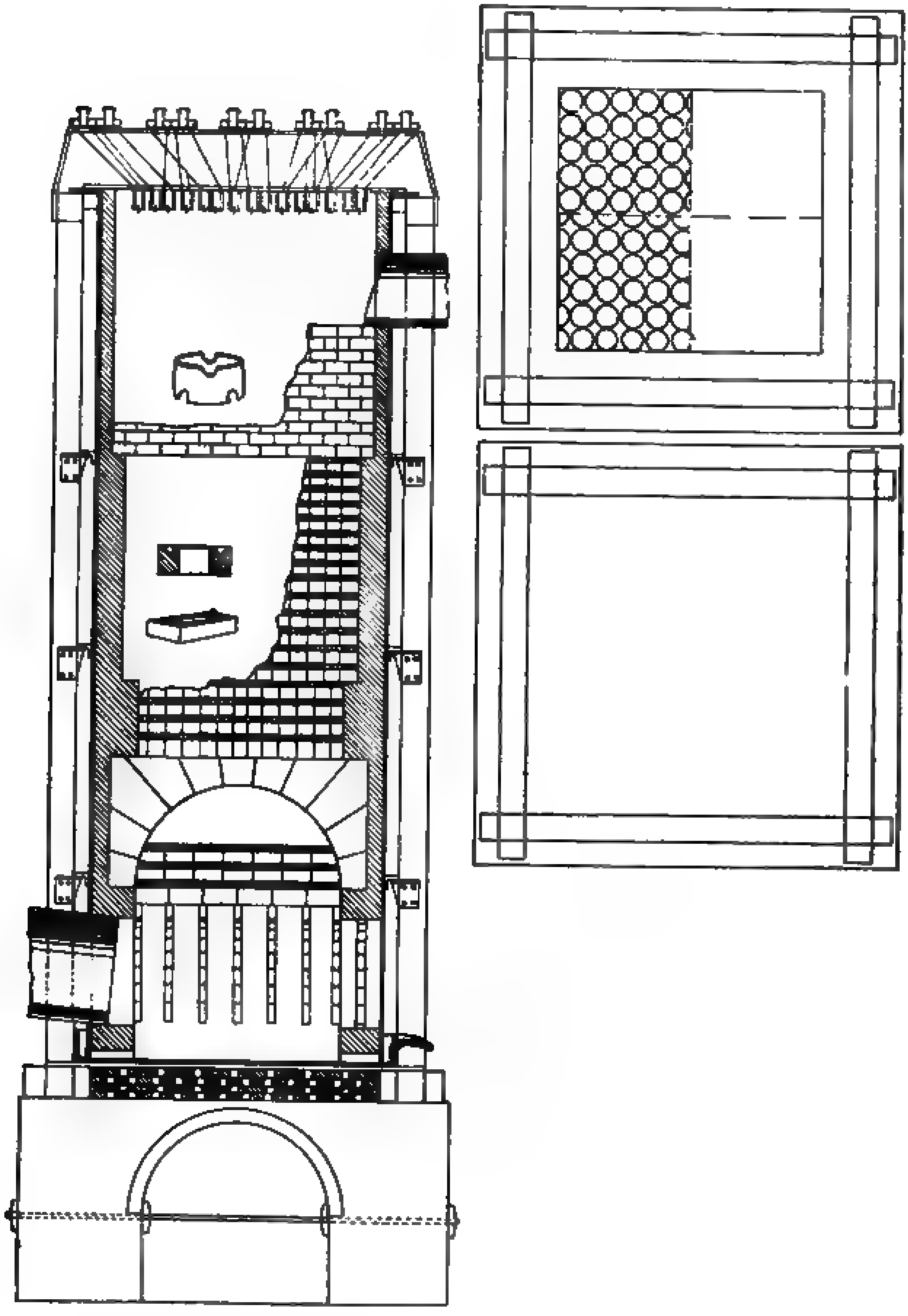

FIG. 1

are allowed to hang within the upstan
erally stated that this is necessary in
contraction. The fallacy of this is ir

are attached rigidly to the heavy inlet pipe for the gases at the bottom of the tower and that no provision is made for the rise and fall of this pipe.

The inlet pipe for the gases presents great difficulties because of its large diameter, the high temperature of the gases and because of the necessity of making the joint tight with the curtain instead of with the heavier and more rigid basin. The pipe conveying the gases from the burners is almost universally made of iron. It is preferably made about 12 to 18 ins. larger than the volume of gas requires and is then lined with brick. At some plants the connecting piece extending into the tower is made of volvic lava, shaped to fit the end of this iron pipe. The volvic lava pipe consists of an upper and lower piece and extends clear through the side of the Glover tower and its lining (see below). A lead or iron pipe is sometimes used to cover the volvic lava and join with the iron pipe from the burner. At other plants a heavy piece of stoneware is used instead of the volvic lava and must be similarly encased. The easier way and one which has proven entirely satisfactory in many installations is that shown in Fig. 126. The heavy iron pipe which conveys the burner gases to the tower is often, and the writer believes should always be lined with brick, and this brick lining is carried straight through the lead connection to the tower, through the lining of the tower to the inner chamber, care being used to lap the brick joints of the lining as tightly and as far as possible. To support this lining during construction and afterwards to give rigidity to the connection with the tower an unflanged piece of iron pipe is inserted as shown and the flange of the burner pipe is rabbitted to receive it.

Tower Packing. Until recently the usual method of beginning the tower packing was to lay a single layer of brick over the entire floor of the tower directly on top of the basin. In harmony with modern steps for the further protection of this basin, the bottom of the tower is now more commonly covered with two or three layers, breaking joints, sometimes split brick being used for the lower layers. For even distribution of the gas within the tower a considerable chamber must be left at the bottom. For this purpose and to support the chief weight of the packing, a heavy lining wall is made up higher than the top of the inlet opening. In large towers several piers, or perforated or arched walls are carried up to the same height, to serve as supports for the grid. It is customary to make this lining from 18 to 24 ins. thick. Above the top of the inlet opening it is then reduced in thickness, leaving a shelf 6 to 9 ins. around the inside of the tower level with the tops of the center piers or walls. In arranging these walls care must be taken to distribute the gases evenly over the entire bottom of the tower and not to obstruct their passage. Resting on these piers and ledges the grid is then laid in place. This grid may consist of deep narrow beams of volvic lava or of acid-proof stoneware. It is sometimes made of a series of narrow arches. The latter construc-

tion is in more common use abroad and the former is believed to be more prevalent in this country. A second grid is sometimes laid across the first to distribute the weight, or a second set of arches to facilitate cleaning out from below. The spaces between the ends of the grid beams should then be filled up with lining brick to prevent the grid pieces from falling over sidewise, likewise where the grids join on a pier or wall. The selection of the brick or tile is a matter of great importance as it is expensive to repack a tower. Selection should be based on actual experience with the material in a Glover tower, or recommendation by an expert. Upon this bridge begins the actual packing of the tower from the chemical or reaction point of view. The lining may consist of large lumps of quartz approximately 8 to 10 in. in diameter at first, and later of smaller sizes. Pumice stone or lava pieces shaped to the sides and filled with graded pieces have been used with great success, also acid-proof brick. Ridges of dust, however, are apt to form on the flat upper surfaces of the brick so that they should always be used on edge. In some cases the deposition of flue dust is very heavy indeed and neccessitates the opening of the towers and the washing down with acid, cleaning out at intervals every one or two years. Properly constructed, however, there is no need whatever of such frequent cleaning. If, therefore, bricks set on edge are used for the lower portion of the packing for the first couple of feet they should be set apart as wide as possible and it is best to begin the packing with specially large tiles. Where lumps of either lava or pumice are used, they should at first be of large size, 12–18 in., and should be carefully laid so as not to obstruct the gas passages and so that the sharper corners are upward to prevent the lodgment of dust. The packing material of Niedenfuhr-Lunge illustrated in Fig. 126 has all the advantages of the brick except economy. In fact, it is better in almost every respect than the brick filling but is probably too expensive for ordinary use. A diamond-shaped brick set on edge and with the edges notched out to rest down over the bricks below, has been very successfully used for this purpose in a number of plants. It leaves practically no surface on which dust can collect, as the surfaces have an inclination of about 60° to the horizontal. The inclined sides of this brick are slightly ribbed in order to produce resting places for the acid and ragged edges over which the uprising currents can pass sharply, pushing out the liquid and exposing as much surface as possible. One criticism to be made of the diamond sectioned brick is that they do not retain sufficient quantities of acid (lack of great porosity) to permit of a gradual surface concentration and diffusion of the weaker acid and to delay the passage of the liquid down through this section of the tower by their absorptive or retaining qualities. In this respect pumice or lava would be more advantageous, but the surface exposed by the diamond shaped brick is many times that which could be obtained by the ordinary rough shaping of lava blocks or lumps unless they were specially dressed to about the same shape and size as the

rhomboidal brick. Like all special packings, however, these rhomboidal bricks are expensive, being approximately 11 cents each.

At the top of the tower the temperature has generally fallen to about 100° C., and it is no longer necessary to protect the lead so carefully from the action of the gases. Nevertheless it is as well to carry a portion of the thickness of the tower lining up practically to the top of the tower; 4½ in. or even 9½ in. is desirable merely as a general protection for the lead and as a semiporous surface for interaction. The actual top plate or lute-plate of the tower is not so subject to heavy wear and tear because it is largely cooled by the incoming acids and being always located somewhat above the outlet from the tower, is at the top of a dead space.

The top plate of the tower is shown in Fig. 126, in which are small depressions or cups located all over the top, arranged so as to occupy little room in order to secure as many such sources of supply as possible with the limited area of the tower top. Each of these cups is, as a rule, oval and provided with a division wall separating the oval into two equal acid receiving cups. At the bottom of each of these half cups is a small pipe extending down into the tower for a few inches and extending up into the half cup for from 2 to 5 ins. according to the taste of the designer. Lead thimbles or short pipes with one closed end and serrated open edges are inverted over these up-standing pipes and complete the liquid lutes. When acid is run into the depression it must fill up for a height of 3 or 4 ins. before acid can flow into the tower at all, and the pipe through which it flows is of such a diameter that it flows down around the edge in a thin stream rather than sucking in with a rush. Any method which will supply all of these half cups, one side with a small regular stream of nitrous vitriol and the other with a small stream of chamber acid, will give us a good distributing system. Ordinary cocks on the pipes to regulate each stream are out of the question as they plug up and it is practically impossible to regulate the size of the stream accurately. The usual system of making the subdivision is that indicated in Fig. 126, where a series of lips are dressed over on one or both sides of a straight or circular trough and each of these lips is permitted to slightly overflow, the size of the stream being easily regulated with very great minuteness by a slight tap or blow above or below on the crest of the lip. Each of these little streams has a pipe to convey it to the proper point at the top of the tower.

On the floor above the head of the tower (in order to secure the head for a constant and steady flow to the towers) is located the tank and generally also the level apparatus. It is customary to make the top and sides of the tower very much lighter lead than the bottom. About 16 lb. lead is generally deemed heavy enough. It is false economy to so reduce the thickness of lead that a renewal of any portion of the tower will be necessary. Good policy demands that the tower be so built, like the "wonderful one horse chaise," that when one piece requires repairing, the whole thing may as well be taken down.

Capacity of Glover Tower. It is found desirable to maintain, at least approximately, a certain fixed relation between the size or capacity of the Glover tower and the size or cubical capacity of the chamber installation. Opinions as to this relation vary somewhat and should in any case always be expressed in terms of actual working volume of the Glover tower and not of the total space within the lead. Experience has indicated that if the tower is properly packed there is no gain obtained by extending the net height of actual packing, more than about 20 ft. Consequently the size will be a matter of variation in cross-section rather than in height. This cross-section has in some cases been as great as 25 or 30 ft. in diameter without detriment to the action of the tower. About 300 or 350 cubic feet of actual Glover tower packing space is allowed per ton of sulphur burned per day.

Acid Coolers. The acid running away from the bottom of the tower and coming from recent contact with the hot gases will as a rule, be very hot (about 130° C.). Even when the burner gases are cool it is about 100° C. It may be higher, but as 60° acid begins to boil, at about 180° C., a much higher temperature than 150° cannot reasonably be expected. Nor is it desirable, because under most conditions all of this acid must be cooled either before storage or before its return to the Gay-Lussac tower for absorption of nitrous-vitriol. For this purpose there are generally located just below the bottom of the towers cooling worms or tanks. Sometimes air coolers are used. As far as possible the hot acid should be kept out of contact with the lead until the latter is cooled on the other side by moderately cold water, otherwise the wear and tear on the lead coolers will be heavy as was explained in describing the corrosive properties of acid, p. 145. Fig. 127 illustrates one of the most convenient devices for cooling of Glover tower acid (where water is moderately scarce). A wooden tank is built cross-divided into a number of compartments, tightened up with bolts and lined with 6-lb. lead. Along one side of it is a lipped trough of stoneware sections backed with asbestos millboard and beaten into an 18 lb. lead trough covered with wood. In each (
nested coil of 1 in. AA lead pipe provid(
or silica funnel extending down into tl
surface of the water. The bottom en
the edge of the tank so that the coil a
various turns of the coil are separated by
in order to make the coil a rigid unit.
with a separate plug in the bottom an
it may be entirely emptied of mud o
or permit the examination of the coil
coil is separately fed by a short syphon
gutter at the back and each discharges
at the front (or back) of the system.

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the syphon-pipe is itself surrounded by sewer-tile or other stoneware pipe sometimes two layers being used and the space between the pipe and the tile packed with asbestos fiber. Similarly the pipes carrying the cold water down to the bottom of the coils may be covered with insulating pipes if this is necessary, but generally no such precaution need be taken. Unless the Glover tower is set very high (so that the space available under it is great) it is preferred not to locate the tank under the Glover because it must be made too shallow for the most efficient working, or the storage tanks beneath the chambers become too low. It is better to allow space (either beside the Glover or between the Glover and the first chamber) on a separate platform about 6 feet below the level of the Glover tower for devices of this character. This brings them nearly on the level of the chamber floor, not more than 2 or 3 feet below it at most, permits the flow of the acid from the cooling devices by gravity to the storage tanks and still permits the elevation of these storage tanks above the ground high enough to locate all acid eggs below them without much excavation.

Storage Tanks. Tanks for the handling of acid are generally made of timber lined with 6 or 8 lb. lead. It is desirable to have in each tank at the head of the tower several hours' supply of acid for the tower in question. The tanks at the bottom of the towers both for Gay-Lussac and Glover acid should have at least a day's capacity and the tanks for chamber acid may have any desired capacity according to the method in which the acid is to be used. These tanks may all be satisfactorily located under the chambers and should be covered or provided with a sub-roof under the chamber floor and located if possible far enough from that floor to allow of access to the floor for examination when necessary. Cooling of the acid is generally required for the Glover tower acid only. In some plants it is thought desirable to cool the Gay-Lussac acid but usually this is unnecessary, unless the Gay-Lussac acid is to be recirculated or a portion of it used in intermediate towers.

Chamber Reactions. Turning now to the chambers, it is well to consider briefly the general types of reactions which are expected to be performed therein. Several theories of the operation have been suggested and it will be interesting to present these and consider them briefly.

Davy, observing the presence of NO_2HOSO_2 crystals and the necessity of water for the reaction, proposed the explanation that $2SO_2+3NO_2+H_2O=2NO_2HOSO_2+NO$ forming droplets in the chamber atmosphere which sink into the acid at the bottom and are diluted thereby, water being condensed on the side curtains in larger proportion and diluting this bottom acid. On dilution

$$2NO_2HOSO_2+H_2O=2H_2SO_4+NO+NO_2$$

which partly oxidizes $2NO+O_2=2NO_2$ again to unite with moreS O_2. The objections to this are that so much more water condensation is not

observed on the curtains and instead of there being much more NO and NO_2 near the bottom they seem to be evenly distributed through the gases.

Berzelius and others including Peligot, Weber, and Raschig regarded the formation of nitrosyl sulphuric as wholly accidental or abnormal.

Lunge, Hurter and Sorel substantially agree that

$$N_2O_3+H_2SO_4 \rightleftarrows 2NO_2HOSO_2+H_2O,$$

calculated the theoretical rate of formation in close agreement with fact, and suggested circulation of drops through varying conditions of temperature and practically constant H_2O and N_2O_3 vapor tension. $H_2SO_4.2Aq$ passes to the central hot zone, is concentrated, takes up N_2O_3 to form nitrosyl, passes to cooler sides, absorbs water decomposing nitrosyl and forming sulphuric 67 per cent near walls at 75° = 27 mm. At center 90°, 27 mm. = 73 per cent. Observations confirm these facts.

The particle of aqueous H_2SO_4 floats about in the chamber gases, being carried up in the middle and down at the sides; on the one hand, owing to the heat of the reaction and, on the other hand, owing to the cooling action of the chamber sides. These particles of acid are alternately subjected to higher and lower temperatures. When the temperature is raised concentration increases by evaporation and the acid is able to absorb or retain greater quantities of N_2O_3. This N_2O_3 when absorbed from the surrounding medium may carry SO_2 in along with it together with water or other constituents necessary to make sulphuric acid. Then on passing over and down along the chamber sides the particles are subjected to a more saturated atmosphere and to a cooling action which tends to condense moisture upon their surface. The moisture may have traveled side by side with the particles for many feet, but not have encountered conditions favorable to condensation. As soon as the moisture is condensed on the particles, thereby diluting them, the nitrosylsulphuric acid is decomposed, liberating the N_2O_3 and forming sulphuric acid which is added to the mass of the particles. Whether this N_2O_3 on its way out from the surface of the particles forms additional sulphuric acid in any manner is not essential, but probably it does not. When liberated, this N_2O_3 travels side by side with the particles, the surrounding SO_2 and the moisture envelope, until the temperature is again raised in the middle zone, when more moisture is liberated from the particles and N_2O_3 is again taken up.

This is at least a clear view of what may go on during the greater portion of the chamber operation. Unquestionably during the early portion of the action at the entrance of the first chamber (when extremely rapid formation of sulphuric acid occurs) Glover tower reactions also occur.

Surface Contact. The importance of surface contact and impingement of gases cannot be denied or overlooked. In 1884 McTear (J.S.C.I.,

'84, 228) carried out an interesting series of experiments by placing a tray 12×12 ins. in the chamber and noting the amount of sulphuric acid collected on the upper surfaces of the tray and of glass plates supported over it. Taking the deposition of acid on the upper surface of the tray alone (700 grams per day) as unity, this deposition was increased 2.3 times by supporting in a vertical position above the tray 12 pieces of glass, 12×6 ins. wide, having a total surface approximately 12 times as great as the surface of the tray. When placed horizontally, 12 ins. wide and arranged as before, the deposition of acid was 4.5 times as great as that of the tray. It was found that a single vertical surface exposed to impingement of the gas condensed about 30 per cent more acid than the other surface and that a horizontal plate collected on both upper and lower surfaces very nearly as much as when placed vertical. This is a purely surface action. As early as 1861 it was suggested to make vitriol in a long channel filled with horizontally supported glass plates, but such an installation would have had too little permanence. Partitions of brickwork, of suspended glass plate and even chambers filled with coke have been tried. Steam aspirators, and even fans, have been used to circulate the gases about in the chambers. But to date the most successful method of mixing and cooling the gases and fixing the suspended liquid is the use of towers between the chambers. These towers may be supplied with a downflow of acid or other cooling means. Thyss and Sorel both attempted to use such towers (in the former case made of lead and in the second case filled with some sort of packing) before Lunge suggested plate towers. Fig. 125 shows in detail what is probably the best developed plate system (George Lunge and Ludwig Rohrmann patented in 1886, 1887, 1889), the plates being placed so that holes do not register and the drops from the edge of one hole strike upon the plate below. Gilchrist has filled the tower with a number of horizontal cooling pipes of triangular section and allowed air to circulate through these pipes. The system has found great favor in many American plants. The smaller sizes of diamond-shaped bricks (rhomboidal packing) offer great advantages of surface and stability. The writer's experience with simpler and less expensive packings, however, has been entirely satisfactory. The tower may be sprayed with ordinary chamber acid, unless the intensive system of operation is to be applied when nitrous vitriol can be profitably used therewith, but too great concentration should be avoided since we have here neither the high temperature nor the rich sulphurous gases to denitrate the strong nitrous vitriol. Re-circulation of these towers with a strength about the same as made in adjoining chambers is recommended.

Cooling also is certainly essential, as the formation of liquid cannot continue without heat dissipation. Cooling is so important that in England a nearly fixed relation between cooling surface (0.2 sq.ft. per cu.ft.) and chamber capacity is recognized.

As the reaction in the chamber progresses to completion, however,

we may confidently predict from the general law of the mass action (common sense) that it will become slower. At the latter end SO_2 (and oxygen) becomes somewhat exhausted, the more exhausted or rare the SO_2 becomes the more infrequent will be the contact of SO_2 molecules with those of nitrosyl-sulphuric acid or nitrogen oxide capable of making it. Thus in spite of any mixing or cooling or other action to which we may submit the gases we can be sure that reactions will be very slow at the end. About 30 per cent of the total weight of acid is made in the first chamber where a number of chambers (4 to 6) are used. Where only three chambers are used this is more likely to be from 30 per cent to 40 per cent and, with only two chambers, may be 60 per cent or even 80 per cent. With the larger number of chambers the last (No. 6) makes only 1 to 3 per cent of the total acid. With three chambers from 9 to 20 per cent of the total acid, and with only two chambers from 20 to 35 per cent or 40 per cent may be expected (these figures are all exclusive of the acid made in Glover and Gay-Lussac towers, the former averaging from 10 to 18 per cent and the latter in the well-operated chambers below 5 per cent).

Sight holes are used for observing the color of the gases for presence of moisture and niter. As the reaction progresses heat is necessarily liberated, becomes sensible as temperature, is partly dissipated by the walls, and gives an excellent indication of the operation. Thermometers are, therefore, very generally used.

Niter Control. As might be expected, niter is the important variable. A temporary cessation of niter supply will cause a rapid fall of temperature in the first chamber, as much as twenty degrees in a few hours, simultaneously affecting the strength of acid produced. The percentage of niter in the gases has the greatest influence on tempreature because within wide limits it controls the rate of production of sulphuric without necessarily at all affecting the yield of acid or the consumption of niter. The simplest indication of niter conditions is the color of the gases. In the first half of the travel (cubical space) white sulphuric mist and reduction by SO_2 to colorless NO prevent any color being observed. About the middle, however, a faint tint (yellowish N_2O_3) and before passing to the Gay-Lussac, in fact in the middle of the last chamber a distinct red (N_2O_4) appears (not a clear red, which means dry gases, but a misty red).

The quantity of niter lost varies much with skill of operating and adequateness of recovery plant to the intensity of working. There is always some loss; never below 1.5 parts per 100 of sulphur burned = 0.5 per cent of the actual H_2SO_4 produced. This figure generally ranges from .75 to 1.25 however. With ordinary single Gay-Lussac and Glover 1.0 per cent is good working and 0.8 per cent is excellent. As the cost of niter is from 10 to 20 per cent of the total manufacturing cost of the acid, careful economy of niter is essential.

One of the first steps in " doctoring " a chamber is to make sure of

ample niter supply. Deficiency is more objectionable than excess and is indicated by paleness of end chamber, decreasing nitrous strength of Gay-Lussac acid, absence of ferrous sulphate test first in middle or end bottoms, possibly by red fumes at exit (SO_2 to Gay-Lussac), decrease in quantity or strength of drips, presence of N_2O in exit gases, etc. The serious consequences are decrease of production, SO_2 escaping to the last chamber in too great quantity with moisture preventing proper formation of NO_2HOSO_2; formation of nitric and further removal of niter from the system, possibly complete reduction to N_2O not recoverable; passage of niter as NO with SO_2 to Gay-Lussac; absence of absorption added to decomposition of nitrous vitriol by SO_2 leading to loss of niter both in bottoms and at exit *because too little* niter is present.

Drips. "Drips" is a name given sample acid collected by troughs from the inner surfaces of side curtains or by trays clear inside the chambers and piped to the outside for testing. It slowly "drips" from these pipes. Weakness[1] of the drip means either too much water (when quantity will be full or excessive) or too little formation of acid (causing lower temperatures and also smaller quantity). Other things being right, the strength of drip serves as a guide to the admission of steam or spray. When the drip becomes too weak the steam supply should be sharply reduced for a time and then resumed. Too much water in presence of excess of oxygen reacts with the lower oxides to form HNO_3, the condensation of which on the chamber side is apt to be injurious. The glass sight-jars, or windows, should not be dripping wet, merely beaded over. Continued excessive supply of steam and consequent formation of nitric acid leads to too much nitric in the suspended acid which is carried down to the bottom acid, weakening the strength of the same and increasing its content of niter by the nitric brought down. This action is cumulative since the weaker acid on the bottom itself tends to hold more nitric. The yield falls off and consumption of niter increases. Action on the lead does permanent damage; white drips result. Also the chamber becomes pale. When the drip becomes too strong it may mean that the chamber is very rich in niter or that there is too little moisture. Another possible evidence of the absence of moisture is the presence of chamber crystals on the glass plates or lute covers. When the quantity of the drip decreases it is sure to indicate either an absence of acid manufacture or an absence of moisture. In the latter case the strength of the drip is apt to be high; in the former case the strength of the drip is low.

Draft. Draft should be primarily regulated according to analyses of gases at Glover entrance and at exit. Too much draft shows at burners

[1] The strength depends largely on the point of collection, 4 to 6° Bé., weaker near the surface of the chamber (owing to the cooling and condensation near the curtain) and stronger from the interior, unless very strong chamber acid is being made, when this difference will be less. It is almost obvious that the absolute strength of the drip is not so important as how the strength varies from day to day and from first chamber to last.

by weak gas, while too little draft is indicated by the absence of O_2. Too much draft weakens the reaction and carries it back too far in the chambers, losing SO_2 and niter. Too little permits over-reduction and loss of niter, finally perhaps loss of SO_2, and certainly loss of profit on the investment. The passage of gas through the chambers as a whole, is observed with delicate pressure gages.

Chamber Construction. The following special principles underlie chamber construction and any chamber detail should be considered with each of them in mind.

1. Variations of pressure inside the chambers may amount to more than $\frac{1}{2}$ in. water column, or about 3 lbs. per square foot over the entire surface of the chamber so that precautions must be taken to prevent the side curtains from sucking in (or bulging) by frequent attachment of both the curtains and the top to a suitable framework.

2. Variations of temperature expand and contract the lead, so curved corners or movable attachments to the framework should be provided to permit movement without buckling or bending the sheets, particularly at joints.

3. The supporting and surrounding framework should be rigid. As the safe tensile strength of lead at 0° or 100° C. is only about 500 lbs. per square inch (a sheet being self-supporting for a height of about 90 ft.), shifting of the framework, failure of supports, or sticking of movable attachments produces destructive strains. In open-sided chambers, wind strains must also be provided against.

4. The corrosion going on continuously, though slowly, is augmented by higher temperature, excessive moisture in the gases, increased niter content, absence of SO_2, too rapid movement or impingement of the gases, or alternate action of liquid acid and gases. The points of most severe attack therefore are as follows: around the entrance to the first chamber, owing to the heat, richness and velocity of the whirl of gases circulating to join the incoming stream; the end opposite this entrance (if the first chamber is not very long) owing to richness and impingement of the entering stream; the whole of the first chamber because the temperature is higher, the gases richer and reaction more active; any points where the sides are uncooled by the outside air, as points in contact with timber framework, the inner sheet of a lap joint, the bottom when it rests on the floor if it is not covered with mud or a layer of liquid, and side curtains where they descend inside the bottom pan; the last chamber where all SO_2 is pretty well exhausted, acid mist is much thinner and where in the absence of SO_2 the reaction $N_2O_4+H_2SO_4=NO_2HOSO_2+HNO_3$ takes place (or with excess moisture even the reaction $2NO_2H_2O+O_2=2HNO_3$).

Most of the chamber plants now in operation have wooden supporting framework of vertical studding crowned with a wall plate rounded on the upper inside edge and beveled away outward below the round. The lead side curtains bend out over the round, are nailed down to the plate

and strapped to the studding. In this construction, seams are generally run vertically and either a large section or the whole side of the chamber, is burned lying upon the floor within the chamber frame and then hoisted into place, or burned at the top and let down after securing the edge to the plate. The side and end curtains being thus placed in position, a movable scaffold the width of the chamber is set up within the walls, the successive sheets of the ceiling are laid upon the scaffold, and the long joints burned three or four at a time. The ends of each sheet extending out over the side sheets where they turn over the plate are burned fast; straps are burned on the ceiling and attached to beams laid as the work progresses. The scaffold is moved along underneath leaving a finished ceiling. For convenience the scaffold is generally made to travel on wheels or rollers. Finally when the last sheets are placed the scaffold is dismembered into sections and removed between two of the side sheets which have been left unburned for a portion of their height. The floor is then well cleaned. The bottom sheets are laid clear across the chamber bottom turning up inside and over a rim of side boarding 18 to 20 ins. high in similar way on all sides, sheet after sheet being burned on as laid. The flues are generally left until the last and give entrance and exit holes for the workmen while engaged in laying the bottom, making the final clean-up before starting as well as testing the tightness of the work.

Fig. 128.

Figs. 128 and 131 show a more modern type of construction (although the wood is still much used) consisting of a steel framework. Chambers of this type are apt to be built of greater relative height and as seen, Fig. 131, a different system of attachment [1] to the framework is used. Incidentally it might be said that this attachment presents many advantages since it can generally be located on the outer face of a joint and the point

[1] In the wooden frame it was noted that the plate is slightly overhung on the inside so that the lead should not touch the framework at any point. To prevent the sucking in by draft, or the pushing out, the entire curtain must be attached by lugs or straps to the framework. Such attachment unless slotted should not be made before the chambers are started up, because the elongation of the lead when heated will throw too much strain upon the straps.

of attchment will therefore be better protected from corrosion within, by the lap. Laps are almost invariably burned on the outside edge so that the extra lead of the lap can serve to protect from corrosion the point at which the joint is made.

Connection of Chambers. In connecting the chambers one with another, circular or rectangular lead gas flues are used. It is generally preferable to make the flues circular because they can then be provided with longitudinal stays of wooden slats, easily enclosed and supported by iron rings. In some cases, however, square flues are much more desirable as a matter of convenience and engineering.

The connections between chambers have generally been taken from the lower portion of the end of one chamber to top of the preceding chamber. A great deal of experience, however, has indicated that it makes very little difference from what point the outlet, or to what point the inlet is taken. The natural circulation of the chambers is very quickly set up regardless of the height at which the gases may happen to be introduced. This is, of course, to a less extent the case when forced draft is used.

In making attachments for connections to the chambers and in making repairs, the curtains and the tops, as well as the connecting flues, may be freely cut into and changed. The greatest care, however, is used to avoid disturbing the bottom basin because of its very great importance in the storage of acid, and because of the extreme difficulty of repairing leaks in the bottom.

The various arrangements for observation, taking of drips, temperatures, level of acid within the chambers, etc., are as a rule scattered at different points throughout the chamber. There seems, however, to be no advantage in this wide distribution of points of observation and in some cases they have been concentrated together. For drawing off the acid from the bottom of any chamber a lead syphon is allowed to dip into the bottom pan whree an alcove in the curtain allows sufficient space for it to stand. Acid is thus drawn from the chamber to a "boot" or pot set in the floor outside and made as high as the side obarding of the chamber bottom. Acid is drawn from each chamber to the chamber preceding it, and a similar boot is almost invariably placed at both the outlet from the later chamber and inlet to the earlier chamber, the boots being connected by a pipe and each supplied with its own syphon. From the first chamber acid is drawn to the supply-tanks of the eggs or lifts to the Glover tower, and to the same or other supply tanks, possibly for use of the concentrating system where 66° acid is being made, though such acid is generally taken from later chambers because acid there is purer. Likewise alcoves are best made at the exterme ends of the chambers for drawing off. The writer prefers a single observation alcove with boot at each end of each chamber. The greatest care is generally observed to avoid making unnecessary holes in the bottom sheet of the chamber or doing anything to disturb the layer of mud

over the chamber bottom and expose the lead to consequent corrosion. For this reason a sheet of glass or piece of thin tile is frequently placed under the bottom of the inner syphon-leg to prevent the flow from disturbing any sediment which may lodge on the bottom of the chambers.

Supply of Water. The steam inlets to the chambers, or water sprays as the case may be, preferably the latter, are located along the top of the chamber and the connections are sometimes carried down to index valves located on the working floor or on a working gallery according to the preference of the designer. If water sprays are used they are preferably located on the top of the chamber, 15 to 30 ft. apart, and staggered. No spray should be used at the beginning of the first chamber where the ample supply of moisture from the Glover is available. Connections may be provided for the last chamber but would rarely be used. Steam is often preferable in the last chamber to sustain the temperature. In some cases special water pumps and storage vessels are used, but the source of supply depends largely on local conditions. In all cases, however, the water should be well filtered in a general filter and in addition a small lead strainer provided with the finest brass wire gauze should be inserted in the water supply line right next to the spray nozzle. The water-luted method of connecting sprays into the top of the chambers is shown in Fig. 129, which illustrates an acid-proof spray[1] in position. *A* is the water supply line, *B* the shut-off cock, *C* the filter cylinder, *D* the removable plug for filter when cleaning, and *E* the lead pipe water-luted at *F* and easily removable.

Fig. 129.

Draft. It has been shown that a certain time is required to complete the reaction to the point when the remaining gases may safely be introduced into the Gay-Lussac, that a sudden increase of draft upsets the operation of absorption and leads perhaps to loss of niter, that a sudden decrease leads to absence of SO_2 and niter or relative excess of moisture and fixation of niter in the last chamber, and that either change of draft leads to variation in composition of burner gases. In order to better overcome the variations of wind pressure and barometric pressure and reduce the operation of the chambers to a smooth and even process variable by intention only, the regulation of draft is of the utmost importance. For this

[1] Made by Schutte & Koerting Co., 12th and Thompson Sts., Philadelphia, Pa.

purpose an automatic regulator is generally located either between the last chamber (or tower) and the Gay-Lussac, or at the exit of the Gay-Lussac.

Special Chambers. Certain special chambers deserve mention and comment. Theodore Meyer utilizes the centrifugal action of gases introduced tangentially into a circular chamber to separate the converted gases from those which have not undergone conversion, the temperature of which has not thereby been raised. The circuitous path, it is claimed, insures better exposure of every particle of gas for a longer period to the action of the nitrous vapors. Fig. 130, Plan No. 2, illustrates the arrangement. Several are in satisfactory operation in the United States and a number abroad but the writer does not happen to know of any that are doing phenomenal work.

F. J. Falding's invention is described as an apparatus for making sulphuric acid consisting of one lead chamber higher than it is long or wide, combined with a Glover tower, means for cooling the reaction products from the chamber and a Gay-Lussac tower. J. B. F. Herreschoff has for fifteen years been advocating the advantages of chambers considerably higher than their width, pointing out that the construction of roof and foundation were substantially the same for any height and that it was the sides and not the top of the chamber which gave most efficient cooling. Great credit is due Falding for his pioneering, even though in no instance does this chamber appear to have achieved phenomenal intensity or economy. It is claimed that, " in the improved lead chambers, the hot gases ascend by convention to the top of the chambers, whereas the lower zone is relatively cold and the mixture of gases may be drawn off from the bottom of the single chamber with the reaction practically quantitatively complete." Fig. 130 gives some extremely good details for attachment of chambers to structural steel frames, together with general elevation and plan of Falding's chamber (elevation 1 and plan 1) as compared with Meyer's tangent system (plan 2 and elevation 2), and with the ordinary style of chambers (plan 3 and elevation 3). The largest chambers in the world were built on this system at Copperhill, Tenn., for the Tennessee Copper Co. A view of this plant is given, Fig. 128. The single chamber effect, however, is subject to too quick variations and consequent disturbance of condition, and does not seem to give better action in any respect.

Niter Recovery. The Gay-Lussac tower should next be considered, for in it as much as possible of the oxides of nitrogen must be absorbed in sulphuric of not less than 60° Bé. in order that they may be returned to the system by dilution and heat in the Glover tower. As the nitrous vitriol supplies about 90 per cent of the niter used in the process, it is obvious that proper means for the recovery of the niter is essential. It has been seen that a reduction in the amount of niter supplied by the Glover quickly reduces the rate of conversion and the temperature in the chambers,

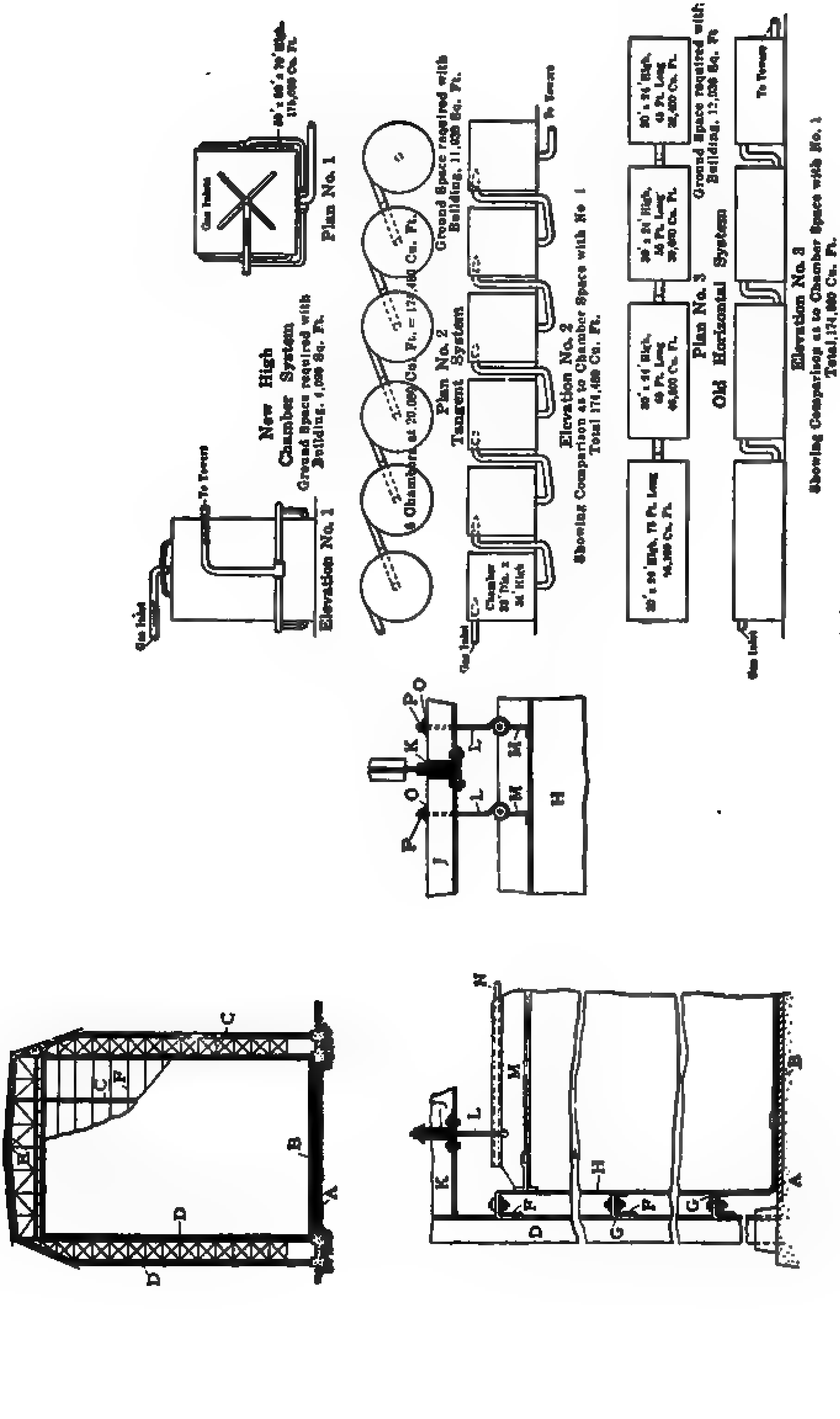
Elevation No. 1
New High Chamber System
Plan No. 1
Plan No. 2
Tangent System
Elevation No. 2
Plan No. 3
Old Horizontal System
Elevation No. 3

FIG. 130.

that if too much SO_2 and moisture are permitted to reach the last chamber, a reaction occurs that tends to tie up niter as HNO_3 in the bottom acid there and that the resulting gases go to the Gay-Lussac poorer in niter, too rich in SO_2 and moisture, thus tending to denitrify the outflowing acid. Not only does this tend to disturb the action of the Gay-Lussac but it tends to weaken the nitrous supply going to the Glover and further reduces the supply to the chambers. The disturbance is, therefore, cumulative. It is counteracted in two ways. Two Gay-Lussac towers are used in series and the flow on the first is made a recirculated flow much heavier than the supply of fresh acid to the succeeding tower or of nitrous vitriol to the Glover. The effect is proportionally lessened. Also a considerable depth of bottom acid is carried in the chambers at about the strength when slight dilution rapidly liberates niter. Not only does the increased mass of this acid serve as a balance wheel, its higher vapor pressure of N_2O_3 supplying niter to the chamber gases when their partial pressure is low, but it also acts as a direct corrective whenever by lack of niter the drips become weak and slightly dilute the bottom acid. Too much emphasis, however, cannot be laid on the smooth and even regulation of the niter supply. One of the objections to potting of niter is that the action is somewhat irregular, whereas nitric acid run into the Glover tower along with the nitrous vitriol can be regularly supplied and instantly adjusted. Similarly the first step toward avoiding trouble is to provide the chambers with an ample stock of niter rapidly and repeatedly renewed by providing them with ample Glover capacity and large Gay-Lussacs.

Dimensions of Gay-Lussac. The dimensions of the Gay-Lussac tower necessarily correspond in a measure with those of the chamber and with the capacity of the burners as well as the method of operation. Intensive working naturally requires the larger Gay-Lussac capacity. One per cent of the total chamber space may be sufficient for English practice of 22 cu.ft. to 29 cu.ft per pound of sulphur. Two per cent Gay-Lussac space may suffice for the American practice of 16 cu.ft. to 22 cu.ft. per pound, but 3 per cent of the chamber space is almost necessarily required for intensive working on the basis of less than 16 cu.ft per pound. As a matter of fact it would be economy in the long run to use not less than 2 per cent in any case and 3 per cent if the method of operating the chambers is to be more intensive than 20 cu.ft. per pound of sulphur. These percentages apply to the space occupied by the packing and its interstices and not to the total space within the lead shell.

Gay-Lussac Packing. The packing of the Gay-Lussac may consist of coke but it is probably true that the best grades of coke occasion a considerable loss of niter. Tile or special earthenware shapes are widely employed and the greatest advantages are claimed for them, but in all probability pumice on the whole gives the best result and only its expense is against it. Whether coke, pumice or stoneware is used the greatest care should be used in its selection. Laboratory tests are not satis-

factory for this purpose and experience with the character of the material in actual tower service should be the only guide to its selection. As with the Glover tower, the supply of acid to the Gay-Lussac should be as regular and evenly distributed over the entire cross-section as possible. With the Gay-Lussac, however, we have only one kind of acid to supply. The same luting principle is used, only the cups are not alternately supplied with a different kind of acid. From the Gay-Lussac the gases are generally allowed to exit directly to the atmosphere or to some large stack if one having the needed spare capacity is at hand. Lunge states that the Gay-Lussac towers need not be lined as are the Glovers. They need not be, but it is frequently considered to be in the long run economical to protect the Gay-Lussac towers from possible mechanical injury and from immediate contact with the gases by a thin lining of a single wall approximately 9½ ins. Some space is thus sacrificed, but in the larger towers constructed these days the proportion of this space is relatively small.

The higher towers require horizontal joints in the lead sheets which cannot generally be obtained long enough to reach to the bottom of the tower. These joints should always be made by lapping and burning on the outside with the lap hanging down on the inside. None of the main vertical joints should be near a corner. The changes of temperature in the Gay-Lussac tower are said to be less than those in the Glover and it is generally stated that the Gay-Lussac sides may well be burned to the bottom pan. As a matter of fact, however, in a properly lined Glover the temperature of the lead shell is not greatly above that of the atmosphere and the range of variation of the lead itself is approximately the same in the Gay-Lussac and Glover. There seems to be no good reason for changing the construction in this respect from that shown in Fig. 126. A similar framework (except higher and therefore stronger) and similar methods of attaching the sides to the framework are used with the Gay-Lussac that have been described for the Glover.

Circulating System. It is now proper to describe in more detail the acid circulating system and the apparatus provided for this purpose. It will be apparent that large quantities of acid have to be elevated to the tops of the towers. Calculation shows that the nitrous gases for their sufficient recovery require that an amount of 60° Bé., equivalent to 60 per cent of the total production of the chambers, be run down the Gay-Lussac per day. In practice this is generally 90 to 150 per cent. When intensive work is used, 150 to 300 per cent is needed. The practical limit is sometimes introduced by the heating and concentrating capacity of the Glover. The denitrating action of the Glover, however, is very largely dependent on direct action of SO_2 (importance of having rich hot gases) and, if the chamber acid is otherwise concentrated or is used up in the works, or is sold, and the Glover acts mainly if not wholly as a denitrator, this concentrating limit is not so quickly felt. The Glover product must be always about 60° (77.6 per cent) or the absorption in

the Gay-Lussac will be unsatisfactory. The chamber acid will not much exceed 53° Bé. (69.66 per cent) and the mixture of acids at the head of the Glover should not be stronger than 58° Bé. (74.36 per cent), preferably less, if it is to be fully denitrated and niter is not to be lost as an impurity with 60° acid shipped or used. This 58° would permit (for the concentration in the Glover of the entire "make" of chamber acid) the admixture of two times this "make" from the Gay-Lussac. Twenty tons 60° acid made per day would thus require 40 tons for the Gay-Lussac and the elevation of 100 tons to the heads of the towers if a single Gay-Lussac were used. Two Gay-Lussacs would mean the elevation of more than 140 tons per day.

Fig. 131.

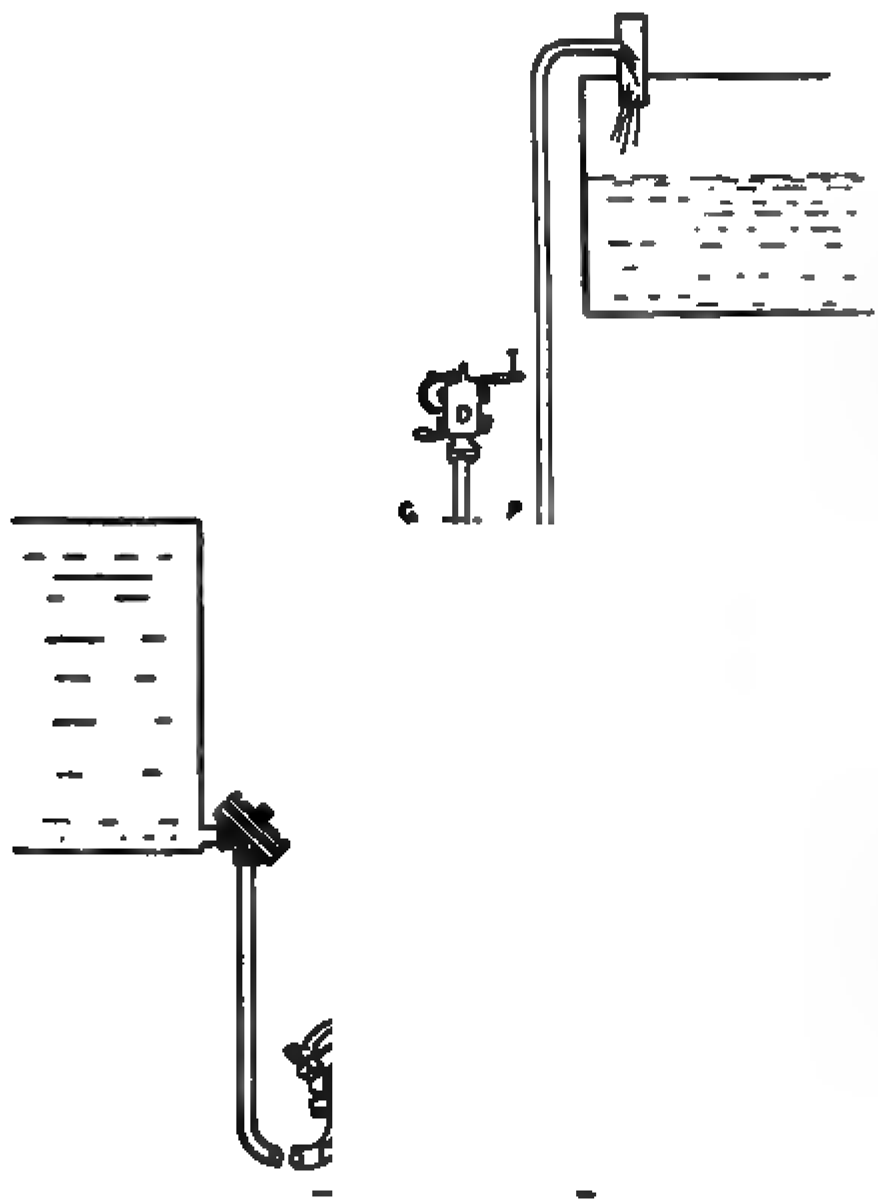

Fig. 132.—Kestner Automatic Elevator.

This lifting has almost universally been done by compressed air admitted into vessels, Fig. 131. These "eggs" are filled with acid through a pipe containing some form of check valve that prevents its return. Air is then automatically or manually admitted through another pipe. A third pipe from the bottom of the vessel permits the acid under pressure to leave the vessel followed by the rush of air of equal or slightly greater

compressed volume than the acid pumped—a method wasteful in the extreme. Fig. 132 shows one of the automatic Kestner lifts attached to a small acid egg, the operation of which will be apparent from the illustration. These Kestner lifts have been used for years by many of the largest acid manufacturers and have given entire satisfaction.[1] Moderately heavy walled lead pipe is used throughout the chamber plant for the transportation of acid. Recently lead-lined iron pipe has found great favor for that portion of the acid lines subjected to very heavy pressure (like those from the eggs to the heads of the Gay-Lussac tower) or to jars by reciprocating pumps or lifts. Geared pumps if made of iron require excessive repairs. Stoneware pumps have not this objection but are hardly safe to use above 30 lbs. pressure or 40 ft. acid-head. Centrifugal pumps, arranged in stages, have been tried with excellent success for low lifts of strong acid but in the chamber work all of the acid is 62° or weaker and the necessity for perfect regularity of operation makes it undesirable to multiply the mechanical devices necessary to accomplish the single lift. Positive acting steam pumps have been used successfully for acid, but are corroded and it is doubtful whether they are any more economical than the best air lifts (Pohlé) where the necessary depth is obtainable. Figs. 133, 134, and 135 show the general arrangement of three different types. Pohlé lifts consume only about half the air required for blowing by eggs, furnish a steady stream like a pump, are without moving parts and can be made practically free from wear. For small installations they are very satisfactory even for lifting by stages when the necessary depth can be obtained without too much expense.

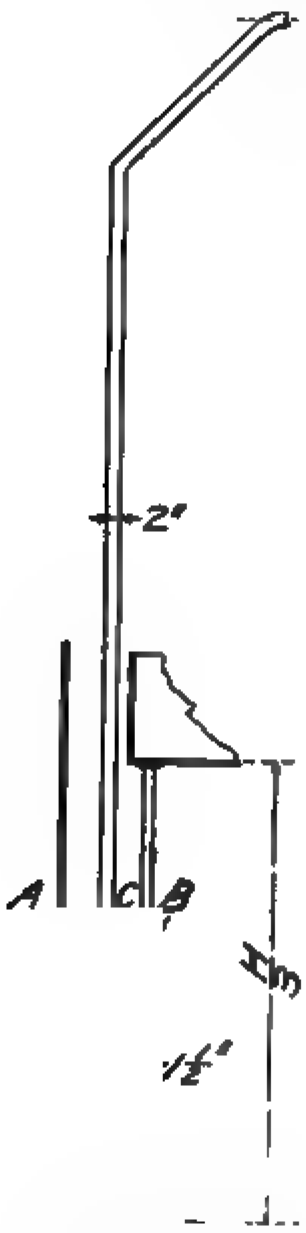

Fig. 133.

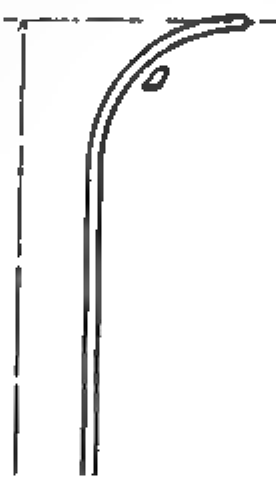

Fig. 134.

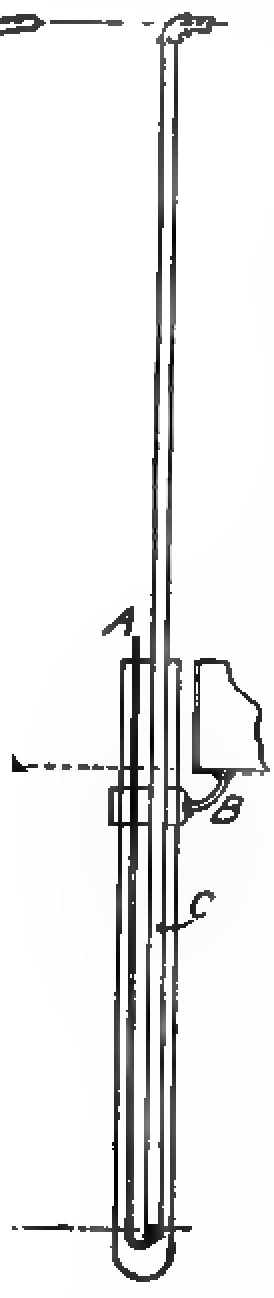

Fig. 135.

[1] They may be obtained from the Bethlehem Foundry and Machine Co. complete with all accessories.

A is the air pipe through which compressed air is carried down to the bottom of a well or shell surrounding the pump pipes. *B* is an acid pipe connected with the tank supplying acid to be elevated. *C* is the pipe for carrying the mixed air and acid up to the point of delivery. The distance from the bottom of the acid tank to the bottom of the well or point of emission of air should be at least one-half of the lift from the tank to the point of delivery. The three different arrangements are substantially the same in general effect but Fig. 135 is to be preferred because by this arrangement it is possible to get at and remove either the air pipe or the acid supply or the lifting pipe without affecting the general arrangement of the whole apparatus. Also at the head of the air lift long curves (*D*, Fig. 134) should be used rather than angles since the shock of the alternate plugs of air and heavy acid frequently causes sufficient jarring to injure the pipe.[1]

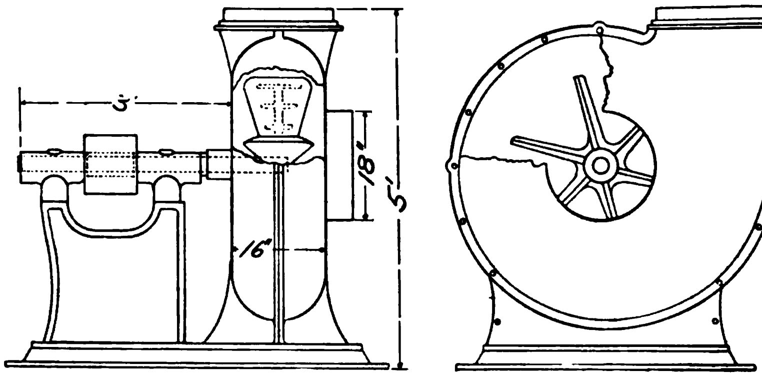

FIG. 136.

Movement of Gases. The fans used for actuating the gases in the chamber system are of three types, according to location, between the dust chambers and the Glover, between the Glover and the acid chambers, or between the acid chambers and the Gay-Lussac.

In the first case a steel fan,[2] water cooled, is used very successfully in handling the hot gases; in the second place a regulus metal fan [3] is frequently used as that illustrated in Fig. 136, and in the third instance

[1] The quantity of acid handled in a large sulphuric acid plant operating on the intensive system, is very great indeed, reaching in some instances 6000 tons a day. Elevation of this acid by the old blowing method would be subject to an almost prohibitive expense, particularly in view of the higher Gay-Lussac towers and the larger general scale of commercial operation. So far the best method of elevating large quantities of acid in the chamber system is that employed by Utley Wedge. This consists of balanced steel mine skips attached to a cable running over a hoisting drum located above the heads of the towers or in an adjacent hoisting house.

[2] Manufactured by A. P. O'Brien, Richmond, Va.

[3] Manufactured by the Sturtevant Blower Co., of Hyde Park, Mass.

a stoneware fan[1] may be used such as is illustrated in Fig. 137. Stoneware fans may possibly be used between the Glover and the first chamber, but the high temperature is exceedingly liable to cause breakage of a fan blade or of the entire blast wheel. Running at such high speed any break might cause very serious damage to the lead flues, or chambers, or both. On the other hand, the regulus metal fan (owing to the heat, velocity and considerable niter content of the gases) is subject to rapid corrosion. Such a fan may also be used between the chamber and the Gay-Lussac but, in this case, there is no objection to using the stoneware fan which is entirely practical and absolutely permanent. In the writer's opinion, where only one fan is used it is best located between the burners (or else the dust chambers) and the Glover tower, and constructed on the O'Brien principle. Extremely satisfactory results have been obtained in this way. Where this is objectionable or where it is desired to operate with a balanced draft (two fans) as recommended by Falding, the second fan can best be located just before the Gay-Lussac tower. For this purpose the writer prefers the larger sizes of stoneware fans.[2]

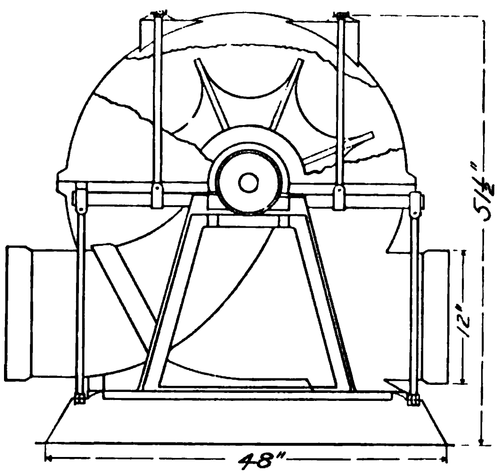

Fig. 137.

Steam jets, formerly considered so valuable, are an extremely expensive means of securing draft and should only be used in case of emergency for which purpose they are best located at the exit of the Gay-Lussac tower. Beyond question, however, much can be done to reduce the amount of power necessary to secure a good draft (if not eliminate mechanical draft entirely) by judicious selection of flue cross-sections and of relative heights of inlets and outlets.

This is particularly the case where the ground configuration permits location of apparatus at very different levels without the building of expensive supports and foundations. When the Glover is located well above the burners, the chambers set high above the ground, when a tall Gay-Lussac is used and open packing employed for these towers with large connecting flues, natural draft is generally found to be sufficient for

[1] The particular fan is selected from the patterns of the Didier-March Co., New York City.

[2] Also manufactured in Germany by Deutsche Steinzeugwaarenfabrik, Friedrichsfeld, Baden, and Vereinigte Thonwaarenwerke Aktiengesellschaft, Berlin.

"moderate" working. "Intensive" working with narrower chambers, intermediate towers, larger percentage of niter to be recovered and two Gay-Lussacs more closely packed, requires forced draft. The use of fines burners and efficient dust chambers further add to the resistance in the path of the gases.

Purification of Sulphuric Acid. Sulphuric acid as manufactured in the chambers, particularly as concentrated in the Glover tower, exhibits certain impurities that are quite important from an industrial point of view. These are lead, iron, arsenic, selenium, antimony, aluminum salts, nitrous oxides and nitric acid, platinum, mercury, the alkalies, calcium, and copper. Most of these impurities can be traced directly to flue dust and experiments carried out during the development of the contact process indicate that practically all of these impurities can be removed by filtration provided other reasons justify sufficient cooling to permit thorough filtration before passing to the chambers. Unfortunately, this prevents the use of a Glover because the gases cannot be satisfactorily filtered unless they are cooler than 200° C. Much, however, can be done to reduce the amount of these impurities by the thorough removal of dust.

Where pure acid is required, however, none of these preliminary means will serve. The acid must be treated specially in order to obtain the desired results. It is found that if the acid is treated with H_2S for the removal of arsenic, practically all other impurities are removed at the same time and the acid is even clarified from some inert suspended matters that are undesirable in appearance only. If, however, a thoroughly pure and limpid acid is required, there is practically no way of obtaining it except by distillation on the one hand or the use of the contact system on the other. Sulphuric acid as made in the chambers will vary in its arsenic content from about 0.1 per cent up to about 0.3 per cent according to the ore used and the amount of dust carried over from the burners.

Where concentrated acid along with battery acid is to be made by the Herreschoff system the easiest way of disposing of arsenic is probably to oxidize it thoroughly with nitric acid and heat, after which the excess of nitric is removed with ammonium sulphate. As, however, the use of the Herreschoff system of concentration is exceedingly limited, two general methods of purifying are most common, both depending upon the action of sulphides liberating H_2S. As acid of 55° Bé. acts directly on the H_2S, decomposing it and giving off sulphur that is extremely difficult to remove by filtration, it is best in carrying out the purification of the acid to have it diluted to about 45° or 48° Bé. Herein lies the chief objection to the chamber process for the making of pure acid. The chamber process should concentrate substantially the entire make to at least 60° Bé. by use of the Glover tower, simultaneously denitrating all the nitrous vitriol from the Gay-Lussac. If purified acid is required, this concentrated acid from the Glover must be diluted

with considerable quantities of water or else the chamber acid must be taken and slightly diluted for the purpose. Then after purification it is practically impossible to concentrate the purified acid by the heat of the Glover tower, even when carrying out the nitration in another Glover, without so far causing the contamination of the acid as to undo all that has been done by purification. This explains why many works manufacturing acid for the general trade have so long retained the old system of purifying acid direct from the chambers and then concentrating it above the burners and finally in platinum stills. Likewise it explains the great progress made by the contact process with manufacturers whose output is distributed widely to the general chemical trade.

After the sulphuric acid has been diluted to the necessary strength, it is submitted to the action of substances producing hydrogen sulphide, or to the action of the gas itself, in large tanks arranged for alternate precipitation and intermediate settling of the arsenic sulphide produced and likewise arranged to be connected alternately with filter tanks where the last traces of this mud can be separated out from the acid. The method most generally used in this country is believed to be the purification by means of gaseous H_2S. This is prepared by the action of sulphuric acid on ferrous sulphide in a heavily built generator, similar in principle to the Kipp.

The hydrogen sulphide gas is supplied to the acid in either of two ways, tanks or towers. The objection raised to the former is that the gas has to be pumped through such a considerable depth of liquid; this seems unimportant when it is considered that it only means making the generator somewhat more resistant to pressure and arranging the gas pipes so that they can be elevated nearer to the surface, when the gas generation is substantially over, to let the residual gas out of the generator. If towers are used, the acid is distributed to their tops in very much the usual way and they are carefully packed with shaped stoneware or brick pieces of approximately triangular section so that no flat upper surface can be presented for the collection of the precipitate. Slight pressure is sometimes used in the tower and generally the exit gases are scrubbed with water or milk of lime to retain any H_2S that might otherwise pass away. The test used to ascertain when purification has been sufficiently complete is the ordinary Marsh test. The acid running down out of the tower is yellow in color and extremely muddy. Sometimes part of the arsenic sulphide is removed by preliminary settling. Others take the entire mud directly to the filter tanks, false-bottom tanks with grid composed of heavy plank covered with lead or acid-proof brick having communicating gutters underneath. In either case the grid is covered first with pieces of quartz and then with finer material until the grade of ordinary sand is reached over which is a perforated lead sheet to prevent disturbing the sand when the arsenic sulphide is removed. The filtering layer thus formed is finally covered with a layer of arsenic sulphide dry.

The acid is run in carefully, not to disturb this layer, and then the level of acid maintained without allowing it to reach the surface of the filter until it is found necessary to empty the filter entirely to clean it. The period for cleaning such a filter is approximately one to five weeks according to the quantity and impurity of the acid used. From the bottom of the tank a down-flow pipe passes into a liquid separator to which suction is applied and out of the bottom of which the acid flows into a liquid lute provided in a tank from 12 to 18 ft. below according to the suction to be used.

A better practice in precipitating the arsenic sulphide is to use separate tanks for the precipitation from those used for filtration and also a final absorption tower. The precipitation tanks are provided with steam pipes for heating and with perforated pipes for introducing the H_2S. The latter are connected from a general H_2S main leading to the generator. Each tank is covered and has a pipe for the unabsorbed H_2S which leads it to a small absorbing tower. Down this tower is run a stream of acid just sufficient to supply the capacity of the purification plant. That is, while one tank is being treated another is being filled by the slow stream of acid from the tower and the rate of filling of the second tank is so regulated that it is ready to treat by the time the other tank is ready to be filled. A set of filter tanks is provided on a considerably lower level. Unlike the usual filter tank these have a large compartment below the filter bed into which the acid is conducted from the tanks above so that the filtration takes place upward through the bed, and clear acid appears above and can be syphoned off at the convenience of the operator. In the precipitating tanks, the treatment can be so arranged as to allow a considerable period for settling and part of the acid can then be drawn off from the upper tanks directly into the upper compartment of the filter tanks sufficiently clear for practical purposes. The advantage of filtration from the bottom upward is that when the filters finally become clogged it is not necessary to dismantle them or remove any of the material. Instead the mud is drawn from the bottom compartment along with some acid into a settling tank from which the clearest acid can be returned for filtration. The outlet from the lower compartment is then switched to a storage tank used for preparing dilute acid for the hydrogen sulphide generator and the water hose is turned into the upper compartment above the filter. The passage of water downward through the filter carries backward out of the interstices all the accumulated arsenic sulphide and leaves the filter substantially clean and ready to start in again on a new cycle.

By this means sulphuric acid containing a total impurity of .05 per cent can readily be obtained. The arsenic is substantially eliminated if the treatment is carried out with gaseous H_2S, falling to about .003 per cent. For comparison it may be noted that the best contact acid contains about .000005 per cent.

Of the various methods used for the precipitation of the arsenic and other impurities by generation of the H_2S within the liquid, probably the best, and certainly the most frequently used, has been the precipitation with barium sulphide. The advantages presented by barium sulphide are two-fold. First, the barium itself is precipitated as sulphate in the liquor and adds greatly to the weight and density of the precipitate. Second, substantially no soluble material is left in the liquor to interfere with subsequent concentration or use of the acid. The acid, however, must be diluted to sp.gr. 1.4 containing 50 per cent of H_2SO_4. To obtain the best results it must then be heated to about 80° C. and a warm solution of barium sulphide 7½° to 8° Bé. run in at the bottom of the vessel in such a manner as to prevent the escape of H_2S. The most convenient way of doing this is to divide the liquid through as many small openings as will permit the passage of the gas without plugging up by formation of the precipitate. These openings may profitably be placed beneath a perforated shelf of lead, or a ribbed shelf without perforations but around the edges of which are serrations to divide the bubbles of gas again. The separation of the purified liquid from the mud may be carried out by either of the usual filtration methods. The only objection presented by the barium sulphide treatment is that the purification cannot be carried so far in this way. Nearly double the amount of arsenic remains in the acid. This can, of course, be removed by subsequent treatment with gaseous H_2S but, if the treatment by gas is to be undertaken, the whole operation might better be carried out by the gaseous method.

The Concentration of Sulphuric Acid. Two systems of concentration, illustrating the wide range of principles employed in practice, will be described.

The first installation, Figs. 138 and 139, will be that likely to be found in a chemical plant manufacturing a good grade of 66° acid; according to methods at the disposal of one who does not control or care to pay royalty upon contact processes. The acid will have been purified in some manner, probably by the use of H_2S gas, and will be approximately 46° Bé. Lump burners will be found of the usual type except that probably the flue above the arches will be somewhat higher at one end.

The common flue above the burner is crossed at suitable intervals with supporting beams, set in reinforced concrete. Beginning with the burner furthest away from the supply of acid, the flue is very low, increasing in height toward the acid supply end. This results from the successive rise of the lead pans to allow for the downward flow of the acid. Upon these protected I-beams are laid cast-iron plates, 1¾ ins. thick at the lower end and 1 in. at the upper end furthest away from the burner arch. Passing backward along the flow of the acid each of the beams is raised 1 in. higher than the preceding. On the iron plates a layer of coarse sand is placed, as thin as can be made with absolute certainty of everywhere

having a separation of sand between the iron and lead in order to prevent immediate contact between them, as these points would thus become overheated and cause excessive corrosion of the lead. Two or three layers of thin asbestos paper may be used instead of the sand. The pans vary

Fig. 138.

gradually in depth from 8 to 14 ins. and vary also in thickness, from 25 to 10-lb. lead being used. After the pans are all in place the long double edges where they abut, are bent over to form lips. The direct flowing of the acid over these lips is not altogether desirable, first because it wears the lip, and second because the 2 ins. left below the top of the pan does

Fig. 139.

not give a sufficient factor of safety in case of temporary obstruction to the flow. For the transfer of the acid under ordinary circumstances, therefore, a small syphon hung in this lip is preferred.

From the series of pans Fig. 139, the acid continues its downward flow into another series of pans Figs. 140–141, which may immediately adjoin the first series or be located in an entirely different building. These pans

utilize the waste heat from the higher concentration apparatus to be described, and are located over the flue supported on perforated cast-iron plates. These plates give a larger output with entire safety and better fuel economy but do not serve to protect the flue below as do the solid plates rimmed around the edge. The acid then flows from the pan to the platinum still, the rate of flow being regulated automatically.

Platinum Stills. Many shapes and patterns of platinum stills have been designed and special advantages claimed for each. In all probability the net result is just about the same in the long run except that the lower and longer pans are more economical of platinum. Some stills are provided with baffle partitions causing a circuitous flow of the acid through the still, the advantage claimed for these being that a better concentration is obtained in a single operation. Against this must be set, not only the small increase in platinum, but also the very great increase in liability to leakage and in irregular strains on the bottom of the pan. Corrugated bottoms are used in some patterns of platinum still. They present about 60 per cent more surface for transfer of heat, but on the other hand, increase to some extent the difficulty of making side joints and consequently the liability to leakage. They have, however, the advantage of stiffening the bottom. Lining with gold has been found to greatly increase the life of the platinum pan and, at the present relative prices of gold and platinum, is a very marked saving. Gold resists about seven times as well as platinum. The gold is not plated on or attached by dipping, but must be attached by the method invented by one of Heraeus' assistants. The overheated gold is poured on top of the platinum ingot heated nearly to fusion, forming a double ingot which is then rolled into the sheet to be made up into stills.

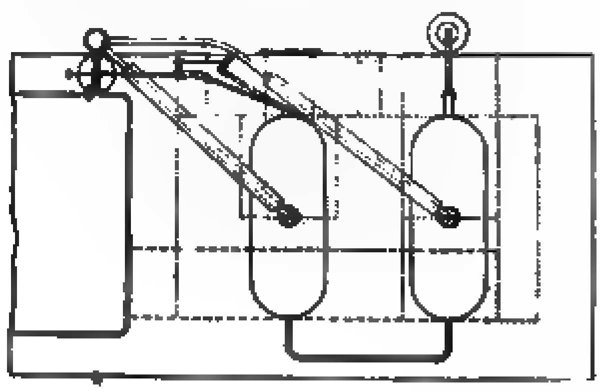

Fig. 140.

Fig. 141.

The chief agents injurious to the stills are the hydrogen, carbon, sulphur and silica (from the fire gases, causing crystallization and brittleness

of the platinum), or mercury (forming amalgam), or iron and aluminum sulphate with traces of calcium sulphate, magnesium sulphate, lead sulphate and silica (from the acid in the stills, forming crusts and tending to cause local overheating, undue mechanical strain, and possibly chemical injury).

The pair of stills illustrated (Fig. 141) with accessories weighs about 100 lbs. and costs $50,000. It will be noted that the fireplace is set somewhat low and ample room given above the fire for the complete mixture and combustion of the gases so that hydrogen and carbon shall have the least opportunity of reaching the still. Furthermore, the ascending gases strike directly against the porous arch from which they are partly deflected through the alternate pigeon-holing which supports the left-hand side of the arch. From there they pass upward under the still in a diagonal direction calculated to avoid the impingement of suspended matter against the bottom of the still and at the same time give the freest possible circulation of heated gases across the bottom of the still. Some authorities prefer the location of the still lengthwise of the flue, as this will better exhaust the heat of the gases. As most installations utilize all the waste heat of the gases in any case under preliminary concentration pans, it is preferred to place the still crosswise of the flue and obtain the contact between the hottest possible gases and the platinum surface throughout, leaving no opportunity for partially cooled layers of gas to linger against the bottom of the still. A second opportunity is then offered the gases to drop whatever dust may have been carried gradually up over the arch and then they again strike diagonally under the second platinum still. From here the gases pass downward into the flue and behind the fireplace into the first described pan-flue. The platinum still is not supported directly upon the brickwork but upon an iron ring and, to increase the efficiency of its distilling action and return as little condensation as possible, it is customary to set the iron ring below the top of the brickwork and to protect the top of the still from cold air by iron plates which may be simply laid on top of the brick setting. The upper still is intended to be fed at about 60° Bé. and the lower still to carry the acid up to 98 per cent if desired, making a distillate of from 60 to 63°, which is returned to the first still.

In the installation shown the distillate outlet pipes were of platinum and provided with iron covers acting as condensers. Platinum stills should be frequently cleaned, and washed out with hot water. Any strong acid left in the stills should be carefully removed before washing.

Where concentration of sulphuric acid is to be carried out in platinum pans, it is desirable to remove the last traces of lower oxides of nitrogen. This is best done by addition of ammonium sulphate, liberating the nitrogen as such. Nitrosyl sulphuric acid reacts with ammonium sulphate as follows: $2NO_2HOSO_2+(NH_4)_2SO_4=3H_2SO_4+2H_2O+4N$. With N_2O_3 the reaction is $N_2O_3+2NH_3=3H_2O+4N$. With nitric acid,

$3HNO_3+5NH_3=9H_2O+8N$. Ordinarily about .1 to .5 per cent of ammonium sulphate is required. It has been found that, while the reaction of nitrosyl-sulphuric and N_2O_3 is rapid, with nitric it is slow. Therefore the presence of nitric acid in sulphuric to be concentrated in platinum should be as far as possible avoided and as an added precaution it is well to add the ammonium sulphate far enough in advance that it may have ample chance to be heated and boiled with the acid for a considerable time before passing to the still. This is most conveniently carried out in the present installation by the addition of the ammonium sulphate to one of the earlier pans. Of course where purified acid is being treated, as in the particular installation described, the addition of ammonium sulphate will hardly be necessary.

Owing to the prohibitive cost of platinum it is being abandoned almost completely in England. Better designed stills with tile lining, Kestner stills, towers, or silica dishes in cascade are rapidly replacing it.

What has been for many years regarded by some as the most perfect type of concentrating apparatus for sulphuric acid, is the still or furnace which was invented by Mr. L. Kessler, securing from the French National Society for the Encouragement of Industry the first gold medal. Since its original development in 1890 the apparatus has been improved in minor details, but it is substantially the same and still remains one of the best for the concentration of sulphuric acid that has ever been developed. Fig. 142 shows the arrangement of the Kessler apparatus. Fig. 143 is a detail of the portion in which the hot gases first come in contact with the acid, and also of that portion of the apparatus in which the preliminary concentration is carried out. In C, Fig. 142, a deep coke fire is built, making it practically a coke producer-gas installation, and ports are provided above the fire for the admission of a regulated supply of excess oxygen for burning the carbon monoxide produced in the coke fire. An excess of this oxygen is allowed so as to somewhat reduce the temperature of the gas and the heated gases are taken through the flue into the saturex at about 900° C. The first apparatus is called the gasogen or gas-making apparatus. It is built entirely of brick properly buck-stayed, provided with a simple and convenient grate and an opening in the top for supply of coke. The fire is built so that it requires attention not more than twice during the twenty-four hours and sometimes only once in twenty-four hours. During this period of replenishing the fire a damper permits

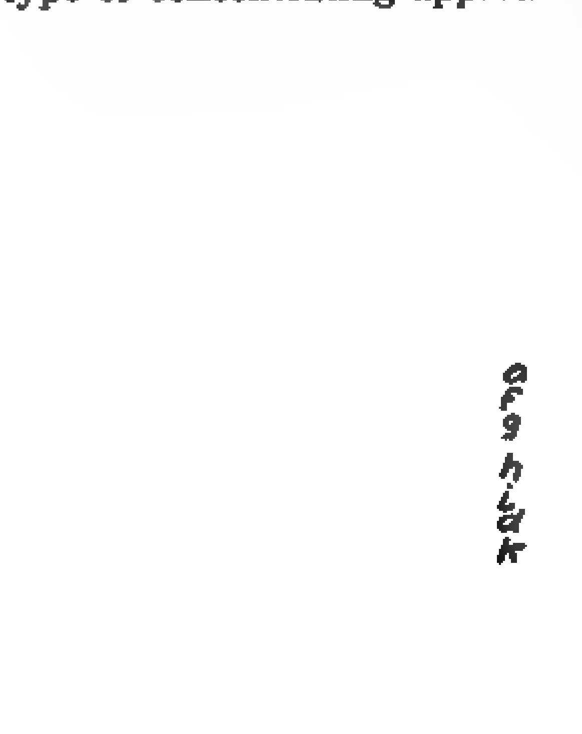

FIG. 142.

entire shutting off from the concentrating apparatus so that any dust formed during this period of disturbing the fire is not carried into the acid. The duration of this interruption does not exceed one hour, and with proper equipment may be completed in half an hour or less, the larger part of this time being given to clearing the fire of dust by allowing

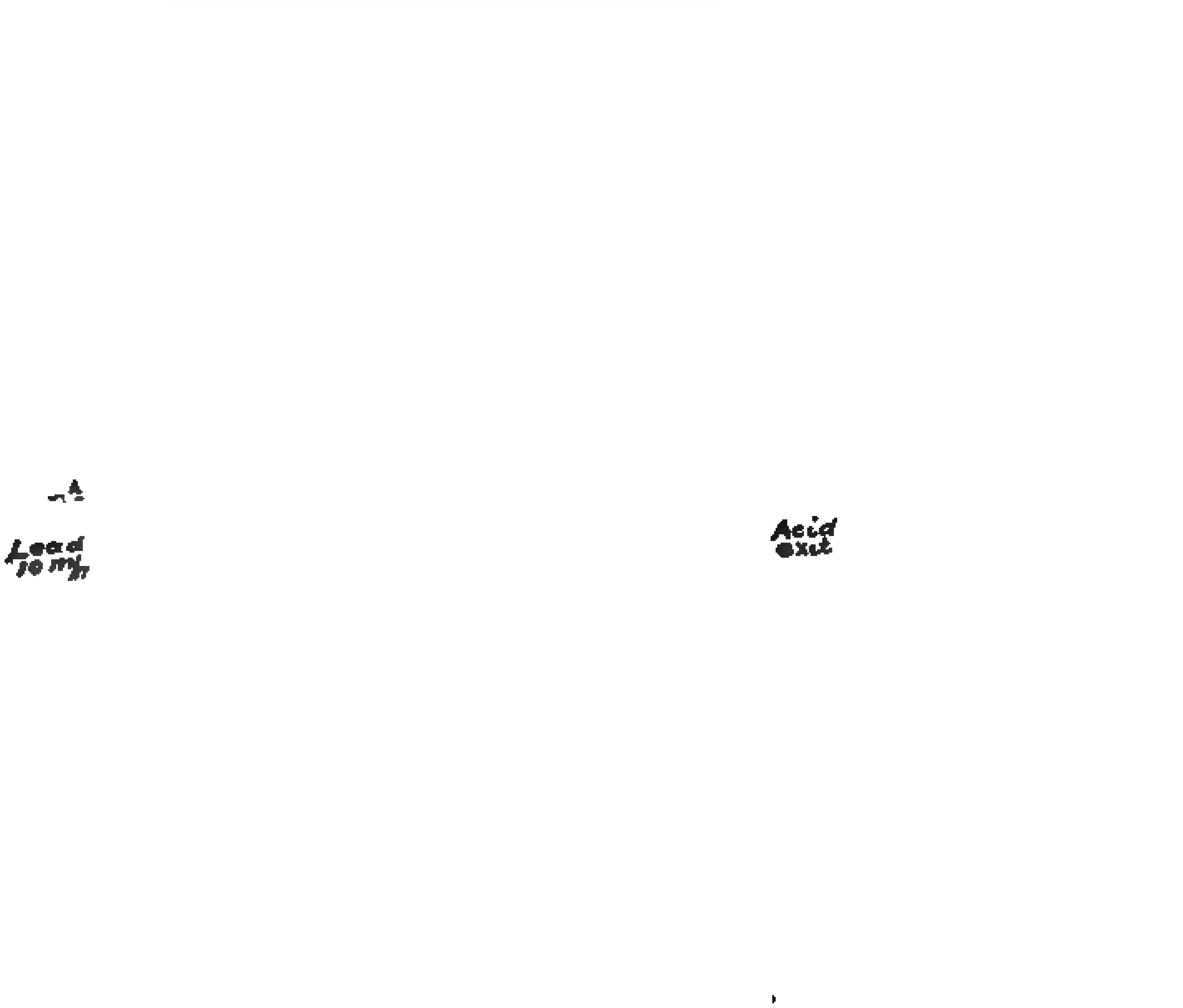

FIG. 144.

it to burn directly up the stack for a few minutes. After the gases above the fire have become clear, the damper is opened and the heated gases admitted directly to the saturex.

The saturex in which the final concentration is carried out consists of a volvic lava box carefully fitted and joined with acid cement, surrounded by a packing of extremely fine quartz sand, all of which is encased in lead. Openings to this box with volvic lava plugs are provided at the points *C*, Fig. 143 so that, with considerable ease, the covering plates may be removed, the plugs withdrawn, and any mud which collected in the apparatus taken out. Supported on blocks set in the bottom of the basin, are partitions extending from the top nearly to the surface of the acid. They are so arranged that the gas entering by the flue cannot pass out of the box through the opening in the cover to the plateau or

preliminary apparatus, without passing under these partitions. Also they are so arranged as to give the greatest length of narrow opening between the bottom of the partitions and surface of the acid. From here the gases, more or less laden with moisture, and containing some suspended or entrained particles of acid and some anhydride fume, pass upward from the saturex into the plateau. The action of the saturex is not generally well understood. As a matter of fact the gases are not merely blown in a thin stream across the surface of the acid, as is generally supposed. Instead, when the draft is started, small waves are made upon the surface of the acid which gradually increase until they begin to touch the bottom surface of the curtain. The instant this happens a rather violent agitation takes place accompanied by strong bubbling and splashing of the acid so that the mixture between the acid and the gases is much more thorough than is generally thought. An enormous surface is in this way exposed to evaporation by contact with gases of very high temperature. The entrance temperature of the gases approximates 900° C., but the evaporation cools the gases so rapidly that there is very little decomposition of the acid in the saturex. In making 98 per cent that boils at 320° C. concentrated acid leaves the saturex at about 240°. Whatever is decomposed is carried up into the plateau and largely recovered, being brought back with the weaker acid. The process of concentration is really one of drying, almost like a partial vacuum concentration, because the fresh gases are continually blown across the surface of the acid and carry away the water with the gases rather than compelling evaporation into a saturated atmosphere. The temperatures throughout the apparatus are much lower than ordinarily correspond to the concentration made. The ease with which 97 or 98 per cent acid may be made and the small amount of fuel required for that purpose, are marked advantages of this type of concentrating apparatus.

The gases passing up into the plateau carrying much entrained acid, some SO_3, with oxygen and traces of SO_2 from the decomposition of the sulphuric acid below, find their way upward only through certain holes in the plateau or shelves, each of these holes being covered by a calotte or hood having a serrated lower edge. The serrated covers break up the gases passing upward and compel them to bubble up through the layer of acid lying upon the plateau. Evaporation is carried out on five successive levels and dilute acid being fed in at the top of the plateau is rapidly concentrated at the same time recovering from the uprising gases practically all of the sulphuric acid which they contain and absorbing some of the SO_3. The contact between the gases and the liquid is so thorough that when the gases pass out, their temperature has fallen to about 95° C. From the top of the plateau column the gases are drawn through the flue into the coke box or filter box *b*, Fig. 142. There they are passed downward through a coke bed which rests upon a grilled false bottom composed of iron pipes covered with lead. Herein are caught practically all of

the suspended particles of H_2SO_4 which have succeeded in passing the plateau, and a slight amount of SO_3 in its suspended condition which is literally filtered out of the gases.

Storage and Packing of Sulphuric Acid. Unless the entire product is to be used at the plant where it is made, it is necessary to store the acid prior to shipment. It is best to store 66°, 98 per cent acid, and oleum in riveted steel tanks generally of large capacity, emptied either through a foot-valve in the bottom surrounded by a low upstand to prevent the drawing of mud, or at various levels through the side, where specially constructed valves having stoneware plugs and seats are used to avoid the gradual leakage that occurs when iron valves are used. As these storage vessels are much too large to permit the application of air pressure for the elevating of the acid, it is customary to locate them on structural steel or concrete supports high enough to run the acid by gravity into cars. It is customary to make these tanks flat bottomed, circular and hemispherically domed. Sometimes lower domes are used to advantage. Horizontal tanks shaped like boilers are used where it is necessary to apply pressure and the storage vessels cannot be elevated to deliver by gravity. For storing acid of 60° Bé. or less, certainly for 50° Bé., lead-lined storage vessels are preferable. These are generally wooden tanks strongly stayed and lined, with 10-lb. lead throughout. In some instances very satisfactory storage vessels have been made by building reinforced concrete tanks, painting the interior of these tanks with pitch and lining the tank with lead. The foot-valve arrangement with porcelain plug and seat can be used in either case. The seat of the valve is set by locating it in place, supported from below by a few strips of wood or similar material, and then pouring in melted sulphur all around it. To make a satisfactory joint great care should be used to have the metallic surface as well as the outside surface of the seat clean and dry and the sulphur should not be too cool. Also the porcelain valve seat should be carefully warmed up so that contact with the hot sulphur does not crack it. These plug valves are operated either by screw stem or by lever. Throughout the works where frequent opening and closing is necessary, and acid distributed through more or less complex lines, asbestos-seated iron plugs or cocks are used with great satisfaction, but should be systematically operated every day. Valves which are not often touched for years and yet which should be ready for emergency service, are much better installed with a stoneware plug and seat in a loose-fitting cast iron socket riveted on the tank bottom.

A blow-off pipe 2 ins. in diameter should be allowed near the center of the tank extending fairly well down away from the manhole plate so that the blast of air which follows blowing the egg into the tank may find free access to the outside atmosphere. Through this pipe a rod or chain may be dropped, or better connected to the float inside the tank and carried over a couple of pulleys to an indicating weight on the outside

of the tank, so that it is practically never necessary to open the tanks in order to ascertain the amount of acid therein and the only occasion for loosening the manhole is the cleaning out of the tank, perhaps once in a year or two. In this manner the corrosion of the interior is very much reduced and the life of the tank greatly increased.

Sulphuric acid is shipped in tank cars, tank wagons, drums and carboys. A tank car is a flat car upon which a steel tank of cylindrical shape is secured on its side by necessary tie rods and end blocks. The capacities of tanks thus used vary from 60,000 lbs. to 160,000 lbs., the thickness of sheet steel used being about $\frac{1}{4}$ in. On the bottom is generally provided a small sump or well into which the "blow-off" pipe dips to empty the tank as completely as possible. Sometimes a foot-valve or cock is provided on the bottom of the tank for emptying, but the better practice is to blow the acid out of the tank with compressed air and to have only a well-bolted flanged nipple on the bottom for cleaning. The tanks are preferably provided with a dome having a manhole plate. Passing to the bottom at one side of the manhole is the blow-off pipe provided with a cock or valve to be shut off during transit, or better with a blanked flange union. Either near to the blow-off pipe or on the opposite side of the manhole plate is the air pipe extending just inside the dome provided with a cock and a cap to protect the threads.

Drums are generally made of light sheet steel similar to glycerine drums. Various sizes hold between 500 and 1500 lbs. of acid. The drums are generally provided on one side with a tapped malleable iron boss, 2-in. hole, with a screw plug served with a lead or asbestos gasket. The carboys in which small quantities of sulphuric acid are shipped, hold about 180 lbs. of 66° acid, consist of glass bottles (10 gals. or 12 gals.) protected from breakage by a casing of some sort. In this country they are generally enclosed in wooden boxes and packed in hay, the packing being thoroughly rammed down under and around the carboy before the cover is padded on and nailed down. Sometimes, particularly for nitric acid, a patented packing is used made of old rubber hose nailed to the inside of the box. Vitrified stoneware cones generally serve for stoppers, being made tight with "putty" or plaster of Paris, and tied down with cheap jute bagging.

The Contact Process. The name is derived from the fact that by mere "contact" with a so-called catalytic material, the SO_2 of burner gases and the oxygen of the residual air are caused to unite to form SO_3, which is then either separated out by cooling (not usual) or absorbed in sulphuric acid of high strength, either maintaining the strength of this acid against the dilution by weaker acid (or water), or else increasing the strength of the absorbing acid above 100 per cent by the absorption of SO_3 in H_2SO_4. When the acid arrives by absorbing SO_3 at a strength at about 106 per cent, equivalent to 26.8 per cent per SO_3 dissolved in H_2SO_4, absorption becomes slow.

The word catalytic is something of a cloak for ignorance. Between the temperatures of 300° C. and 900° C. the mere presence of platinum in a finely divided state, or platinum black serves to very greatly accelerate the reaction $SO_2+O \leftrightarrows SO_3$. At first sight the platinum black appears to take no part in the reaction. It merely glows and gives off heat. The action starts about 325°, and is most complete between 400 and 450°. Similar but less effective results are obtained at higher temperatures with ferric oxide, particularly ferric oxide containing a little copper oxide; also chromium oxide and even hot silica and quartz assist the rate of progress toward equilibrium. It may seem that none of these materials takes part in the reaction, but probably each of them does in one way or another. Particularly is this the case with oxides of iron, copper, chromium and with the sulphates of alkalies and alkali earth metals. In the light of more recent knowledge, the original meaning of "catalytic" must therefore be abandoned or modified to the extent that a catalytic reaction may be defined as a reaction which leaves one of the assisting compounds substantially unaltered after the completion of the reaction. According to the law of mass action such a catalyte or intermediate reacting compound is not to be expected to affect the ultimate equilibrium of the reaction, that is, the final extent to which the reaction proceeds in an infinite length of time. The function of the catalyte is merely to affect the rate at which the reaction proceeds, and thus to give it sufficient rapidity to be of practical interest. Sulphur dioxide and oxygen unite to some extent (at a very slow rate at 350° to 375° C.) whether or not a catalyte be present. The presence of a suitable catalyte (possibly acting as a carrier of oxygen, similar in effect to the lower oxides in the chamber process) greatly increases the rate of reaction so that the sulphur dioxide and oxygen at 375° to 450° combine rapidly and produce sulphur trioxide with nearly theoretical completeness.

We are apt to think of the contact process as the development of the last twenty years, overlooking the enormous amount of effort that for nearly a century was spent in the right direction, but just missing some little step which was important. Until about 1870, however, there was no great commercial demand for very strong sulphuric acid. Then the demand came with the invention of alizarin, followed by the rapidly increasing demand for the artificial product. In 1875 Clemens Winkler published some of the results of his efforts, discussing first the inadequacy of the old methods of producing fuming acid (distillation of sulphates) and then his own attempt to synthesize SO_3, recommending platinized asbestos for the purpose, but making an error which possibly delayed the development of the contact process more than twenty years. Contrary to Guldberg and Waage's law of mass action, even then well known, he stated that stoichiometric proportions of gases should be used. As a matter of fact, we know to-day that it is the excess of oxygen present with these gases, which gives us as complete a conversion as is now commer-

cially obtained. We know also that the presence of the nitrogen has little effect, merely serving to dilute the gases slightly, placing them under a less partial pressure and only in that way slightly affecting the completeness of the reaction. For twenty-five years his error was repeated in one text-book after another. Winkler himself, however, pursued his work technically at Freiberg, much more rationally than any of his publications indicated. In 1878 he used sulphur dioxide and air an in 1881 already had large plants in operation and continued to perfect the process till 1890 or later. In 1881 Knietsch took up the work at Ludwigshafen on the Rhein, and in 1896 patented the cooling of the contact chamber to remove the excessive heat of reaction which causes a reverse reaction, decomposes SO_3 and prevents complete conversion. Equilibrium was reached almost as quickly, with more complete conversion into sulphur trioxide, and the heat was used to preheat the incoming gases. Also quite independently of Winkler at Freiberg, Knietsch showed the influence of numerous impurities that occurred in burner gas from the continued activity of the platinum contact mass and devised a very complete method of purifying burner gases which was patented by him in 1898. Somewhat similar work was carried out more or less independently by Herreschoff and Ferguson in this country a year or so later. About the same time Clemm and Hasenbach developed the iron contact as a first stage of conversion combined with the platinum contact as a second stage.

These investigators showed that arsenic trioxide and arsene poisoned the platinum contact mass, largely reducing its powers of conversion until after the arsenic has been removed. The iron contact mass is not injured by the presence of some copper or even a considerable amount of arsenic, but on the contrary its activity is increased. On the platinum mass the volatile compounds of selenium, antimony, lead and some other metaloids, have a poisonous effect though less marked.[1] Chlorine, hydrochloric or hydrofluoric acid temporarily reduce its activity; silicon tetrachloride deposits silica which, like dust or any other suspended matter, covers the contact mass from ready access to the gases. Two great difficulties, therefore, stood in the way of carrying out the reaction completely, i.e., to the extent of 95 to 98 per cent of the theoretical, and its commercial application. These were; first, the heat generated by the combination of the gases, tending to elevate the temperature of the gases to such an extent that instead of continuing their union, they reached equilibrium between dissociation and union owing to elevation of temperature; second, the poisoning or inhibiting action of impurities upon the platinum mass, these impurities being brought over in the gases from the burners.

Construction of Contact Plant. In order to illustrate the various

[1] For the best detailed discussion of the Contact Process, see Lunge, "Sulphuric Acid and Alkali," third edition, Vol. I, part 2, p. 975.

principles used in the construction of contact plants, it would be necessary to describe a number of different plants more or less in detail provided actual installations were used to illustrate the principles. Instead of that a typical arrangement of the installation is given in Fig. 144, in the form of a schematic diagram which will be described in detail and which illustrates the principles used in the majority of the contact plants in this country and it will then be indicated what portion of this installation can be left out to operate under various separate principles that are in use.

Air enters at the opening A into a drying tower B filled with quartz or other loose material down through which strong sulphuric acid is flowing. The air passes up through this tower and on its way is almost completely dehydrated. It then passes down by the pipe B_1 to the

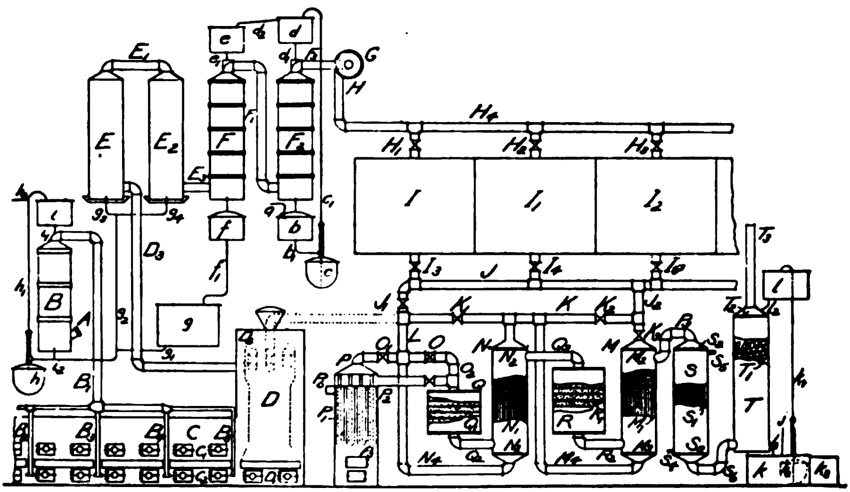

FIG. 144.—Diagrammatic Contact Plant. x

pyrites burners C into the cinder pit under which it is admitted by the pipes B_2, B_3, B_4, etc. The doors of these burners C are of two kinds, upper and lower, the upper being for the insertion of the pyrites and the lower for the removal of the cinder. Both of these should be made as tight as possible by the use of asbestos gaskets and screw spiders or similar devices. Through the flue above these burners the gases pass into a contact shaft D where they pass over the cinder produced by the burners. This cinder is removed through the doors C_2 from the burners, is screened in order to remove dust and a portion of it is then put in through the funnel into the contact shaft D. About 10 per cent of the cinder is used to advantage in this way. The necessity for renewing the cinder arises through the accumulation of dust in the interstices and the fact that the cinder gradually becomes so saturated with arsenic and other impurities that it does not react promptly. The chief consideration, however, is the reduction of draft by stopping up of the inter-

stices with dust. A portion of the cinder may then be shaken down into the cinder pit of the contact shaft and removed by the door D_1. By the heat of the gases direct from the burners this contact shaft will be maintained at a temperature between 600° and 800° C. and in order not to have the temperature fall too low, the shaft is jacketed as well as possible by somewhat heavy walls of brickwork and other devices. As the whole burner system and contact shaft operates under suction, it is preferable to enclose the entire setting in a steel plate cover closely riveted and caulked. In this contact shaft the gases are partly converted, about 40 to 50 per cent of the SO_2 present when they leave the burner chambers being changed over into SO_3, and sufficient heat being generated by this reaction to maintain the temperature of the gases. Leaving the contact shaft by the pipe D_3, the gases are somewhat cooled and are introduced into the cooling tower E. This tower consists of a riveted steel plate shell over the outside of which water is poured, the water being collected in a trough at the bottom and carried away. Some acid condenses in the pipe D_3 and runs into the tower E. Also considerable acid collects in the tower E and is removed by the pipes shown at the bottom. One such tower, unless of considerable size, would be insufficient to cool the gases so that they pass through the pipe E_1 into a second tower E_2 (or third) of similar character, whence thoroughly cooled they pass by the pipe E_3 into the absorbing tower F. This tower consists of either riveted steel plates or semi-steel castings, or cast iron poured into a mold containing a wrought-iron outer shell. The reason for this precaution is that cast iron is affected by SO_3 in a peculiar way, the SO_3 seeming to enter into the pores of the cast iron and cause a gradual expansion, placing the metal under such strain that it cracks or even bursts apart as mentioned on page 145. The tower F is filled with quartz or similar surface-exposing material and is fed from above with a slow stream of acid for the purpose of absorbing the SO_3 in the gas. From the tower F the gases pass on to the pipe F_1 into the tower F_2 which is of similar construction and likewise provided with a flow of acid, the strength and character of which will be mentioned later. Thence through the pipe F_3 the gases pass to the blower or actuating means for the system, the part of the apparatus hitherto described being operated under suction. From the blower the gases pass by the pipe H to a series of valved branches H_1, H_2, H_3, etc., leading into filters I, I_1, I_2, etc. These filters are mere boxes of iron or lead containing a deep layer of fine coke, or fine slag from the basic open hearth process. In either case the action is largely one of gaseous filtration, in order to remove the last suspended impurities that have not been taken out by the washing or the centrifugal action of the fan. This purification is so thorough that the gases no longer betray the presence of the dust in a strong beam of light nor do they yield up any impurity to filtration by a close plug of cotton wool. If there be suspended sulphuric acid left in the gases they will blacken the plug of

cotton wool, or if any traces of dust remain these will be deposited upon the cotton and show their discoloration. The number of filters are thus placed in parallel in order to permit the cutting out of one filter by closing the entrance and exit valve and the renewing of the filtering body without interruption of the process. From these filters, the gases, thoroughly purified, pass away through the valved connecting pipes I_3, I_4, I_5, etc., to the assembling gas main J. From here two courses are open to them, but the normal course used as a rule throughout the operation of the plant will be first described and the emergency course J_1 described later. Normally the gases pass through J_2 downward through the valve K_3 into the heat exhanger M. This heat exchanger is constructed very much like a tubular boiler having the tubes M_1 connected between headers M_2 and M_3 and the incoming gases pass downward through these tubes and out of the heat exchanger by the pipe M_4 up to the distributing main K. During the passage through the heat exchanger M they have been partially heated up by the hot gases passing away from the platinum converter R. They are again heated up by being passed down through the heat exchanger N of similar construction, having the pipes N_1 between the headers N_2 and N_3 outside of which pipes are passing the hot gases from the first converter Q. The now thoroughly heated gases leave the heat exchanger N through the pipe N_4 and pass upward into the pipe O and downward through O_2 into the converter Q. This converter consists of a cylindrical cast-iron box containing a number of layers of platinized asbestos supported on punched sheets of steel. The gases passing down through this platinized asbestos are further converted and heated by this action. They then pass away through the pipe Q_2, and around the pipes N_1 and are cooled by the incoming gases passing through the inside of these pipes. From this heat exchanger they pass through the pipe Q_3 into the second platinum converter R having similar layers of contact material R_1 supported on steel trays. This converter may be somewhat larger in order to insure the complete conversion of the now nearly exhausted gases. From here they pass through the pipe R_2 into the heat exchanger M, where they pass around the outside of the pipes and give up some of their heat to the incoming gases, passing down through the pipes. Leaving this heat exchanger through the pipe P_3 they pass the final cooler S which is again constructed somewhat like a boiler having headed pipes S_1 between the headers S_2 and S_3, only in this case instead of being cooled on the outside by gas these pipes are cooled by water fed through the pipe S_4 and overflowing to the pipe S_5. The now thoroughly cold gases pass through the pipe S_6 into the absorbing tower T. This tower is filled with porous or other acid-proof material and is sprayed with acid from the distributor T_2 after which the gases are permitted to exit through the pipe T_3 to the atmosphere.

The passage of the various liquids used for treatment of this gas should now be traced. The acid for absorbing sulphur trioxide from the

iron conversion enters through the pipe *a* to the tank *b* at the foot of the tower F_2, and adds itself to the liquid flowing down from the tower. Thence it flows to the pipe b_1 into the egg *c*, and is thrown up by the pipe c_1 into the tank *d* at the head of the tower. The acid added by the pipe *a* should be of such strength and quantity as to maintain the flow of acid down the tower F_2 somewhere between 93 and 99 per cent, preferably about 97 per cent, because the absorption of SO_3 is much more rapid and complete in sulphuric acid between 97 per cent and 98 per cent than in acid which is either much weaker or stronger. From the tank *d* most of acid is permitted to flow down the tower F_2 but as the acid increases in quantity through the absorption of sulphur trioxide on the one hand and the addition of weaker acid from the pipe *a* on the other hand, the overflow goes to the supply tank *e* of the tower *F*, whence the acid trickles down in a slow stream through the tower *F* and may be raised to a strength equivalent to 105 or 106 per cent H_2SO_4, and be taken to the finished acid tank *g*. Calling the acid 105 per cent means that the sulphuric acid contains sufficient sulphur trioxide dissolved in it that, when the necessary water is added to unite with this sulphur trioxide and produce sulphuric acid, the total quantity of acid of 100 per cent produced will be 5 per cent greater than the amount of H_2SO_4 and SO_3 taken. The strength may likewise, of course, be expressed by giving the percentage of free SO_3 dissolved in the H_2SO_4. The acid collected by condensation in the cooling towers *E* and E_2 will be impure owing to the amount of dust carried over from the iron contact shaft and may profitably be used in the preliminary drying tower *B* flowing down the pipes g_3 and g_4 into the egg *h* whence it is blown up by the pipe h_1 into the tank *i* at the head of the drying tower. The excess of the drying acid thus accumulated may be flowed over to the pipe h_2 and utilized for any convenient purpose in the works. A deficiency of acid from these cooling towers is made up from the finished tank *g* by adding acid through the pipe g_1.

The absorption of the sulphur trioxide produced by the platinum contacts *Q* and *R* may be completely carried out in a single tower *T* provided the strength of the acid in this tower be maintained at the most advantageous point between 97 and 98 per cent. A steady flow of weaker acid is taken in through the pipe *j* to the tank *k* where it is cooled and thoroughly mixed with a stream flowing out through the pipe l_3 from the tower. From a special compartment of this tank or an independent tank located beside it, k_2, the acid is thrown up by a centrifugal pump or other convenient means by the pipe k_4 into the supply tank *l* at the head of the tower, whence it flows through the pipe l_2 to the distributor within the tower. A heavy stream of acid is carried in order that the sulphur trioxide absorbed may not too greatly increase the percentage of the acid on its way down the tower. Whatever excess of acid is formed in this system, as in the other, overflows to the tank k_3 and

is regarded as finished acid. Owing to the careful preliminary purification of the gas this acid is a very much purer than that produced by the iron contact. In some plants, therefore, the iron contact is not used and the gases pass directly from the burners into a large cooling chamber that takes the place of the towers E and E_2, after which it is washed with sulphuric acid as in the towers F and F_2, which without the iron contact does not increase the volume of the supply liquid materially because there is no sulphur trioxide to speak of. By using stronger sulphuric acid in the tower F_2 the gases are thoroughly dried and are prepared to go to the filters. The complete conversion is carried out in two steps in the converters Q and R and all of the sulphur trioxide produced is then absorbed in the tower T by 97 to 98 per cent acid. In such an installation the parts D, B, h and i would be omitted as the preliminary purification of the gases has been shown to be more effective if the gases were moist. In fact moisture is injected into them as they leave the burners and before they are cooled in the large chamber which according to that method of working would replace the cooling towers E and E_2.

In the other method of working the gases instead of passing through a more complicated conversion like that shown would be heated by exchange with the gases as they left the iron contact D, and would then be taken directly to a single platinum converter which might be located between two iron contact shafts or in any other convenient position for sustaining its temperature. The second stage of the absorption of the gases sulphur trioxide thus produced might, of course, be carried out in a second set of absorbing towers similar to F and F_2. If a very complete conversion is to be made in the final platinum converter the temperature must be carefully regulated and provision made both for additional heating of the gases and reducing the amount of heating action. When it is necessary to increase the temperature of the gases passing through the first converter Q as for instance in starting up of the plant, the heater P is available and provision is made through the valve O_1 and P_2 for passing the gas through this heater into the pipe O_2 by shutting the valve O whenever this is desired. The heater P consists of an ordinary coal heater of special design provided with the firing door P_3 and having inside heating pipes P_1 and a stack for exit of the coal gases, P_6. When, on the other hand, it is desired to reduce the temperature of the gases passing through the first converter it is possible by opening the valve J_1 to admit cold gases directly from the pipe J into the pipe L and thence into the converter. When a less violent cooling action is desired the valve K_2 may be opened and the gas admitted to the pipe K before passing through the heat exchanger N. It will be obvious that the purpose of breaking up the conversion into a series of stages is to reduce the amount of heat liberated at any particular stage and avoid the necessity of cooling the gases during conversion. It amounts substantially to using a weaker gas at each stage in the conversion. Another method of

getting at the same result is to make the converter Q very much wider and allow the radiation from the thin layer of contact material at the top to preheat the gases to such a degree that the contact mass itself is sufficiently cooled by radiation to the upper portion of the converter in which the gases are being heated. Another method of securing this result is to construct the converter like the heat exchangers N and M and to place the contact material within the tubes, passing the gases on their way to the contact around the outside of the tube so that the mass in the tube is continually kept cool by the passage of the gas around the outside. This was the method devised originally by Knietsch for maintaining within the contact chamber a temperature which at the hottest portion of the chamber should be between the composing and decomposing temperatures of sulphur trioxide. This most elegant form of contact chamber which combines within itself the converter proper, and the heat transferrer is illustrated in Fig. 145. The gases, after leaving the burners and being mixed with steam and cooled in a large cooling and settling chamber designed to take the place of the towers E and E_2, Fig. 145, were then washed as in towers F, F_2, the washing being repeated in successive towers until the gases no longer showed any impurity. Special washing liquid might be used for different characters of special impurities depending on the kind of ore used and they were then finally dried in a tower like F_2. Such gases were then passed directly in through the opening A, Fig. 146, whence they were permitted to circulate back and forth across the outside of the pipes B extending down through the chamber and finally reaching the bottom of this chamber to pass upward through these pipes themselves and to the contact material supported in layers within these pipes. As the gases became heated on their way down to the end of the pipes and as the reaction at this entrance was more violent, the temperature at this point rose to the desired degree and the conversion proceeded very rapidly. Then as the gases passed on through the contact material contained in the pipes they would find cooler and cooler layers of contact materials so that their equilibrium might be retained at its most complete stage, at approximately 400° to 425°, before being removed from the pipes. In this manner 90 to 95 per cent or even 97 per cent of the SO_2 may be converted in a single converter, and if desired, the temperature of the gases can be raised partly by an added exterior transferrer, through which the converted gases pass on their

FIG. 145.—Knietsch Contact Chamber.

way to being finally cooled and absorbed. The final cooling may take place in a separate cooler, *S*, Fig. 145, or the absorption liquid may be so rapidly cooled that the hot gases can be cooled and absorbed simultaneously. If strong oleum is to be made, however, they should first be thoroughly cooled. If 98 per cent acid is to be made a single absorbing tower may be used, but if oleum is to be made it is more desirable to carry the absorption out in a series of towers the last of which is supplied with 97 to 98 per cent acid in order to make an entirely complete absorption.

Broadly speaking, it may be said that the cost of manufacturing sulphuric acid by the contact system is not much, if any, higher than that by the chamber system. The operation is somewhat more sensitive and delicate and involves the use of more refined machinery, so that a higher class of labor has to be employed. The conversion when the contact system is operated properly is practically as complete as that in the chambers. Well designed, the contact system requires practically no fuel for preheating the gases and the power required for driving the gases through the more resistant series of chambers used in the contact system is more than made up by the absence of niter consumption. The cost of installation is somewhat higher owing to the considerable quantity of platinum used, hence the attempt to substitute other materials as oxide of iron, but it is doubtful whether in the long run the substitution works any economy. One advantage of the contact system, particularly where platinum alone is used, is the great purity of acid resulting from the necessary thorough purification of the gases, but for ordinary manufacture of sulphuric acid, particularly in districts more or less remote from foundry and machine shop facilities, there is considerable question whether the contact system offers great inducement to the manufacturer.

VIII

NITRIC ACID

WILLIAM M. GROSVENOR

Occurrence. The usual commercial strengths of nitric acid are "38°" (56.5 per cent), "40°" (61.4 per cent), and "48°" (91.4 per cent). "Pale acid," "free from lower oxides" (that is, less than 0.1 per cent of NO, N_2O_3 and N_2O_4) may be of any strength, but is generally made from acid stronger than 40° Bé. (sp.gr. 1.381) by dilution because the weaker acid does not "bleach" well. "Red acid" is generally 40° Bé. or stronger and contains dissolved lower oxides. "Dynamite acid," is strong acid for making 96 per cent mixed acid (34 per cent HNO_3 and 62 per cent H_2SO_4). It was formerly necessary to have the nitric acid 93 per cent, but now that "oleum" is used, it need only be 88 per cent. "Spent acid" is the mixed acid diluted and partly deprived of HNO_3 by use in nitrating organic substances; and "fuming nitric," is very strong acid containing much lower oxides. "Weak nitric," generally applied to acid 38° Bé. or less, obtained from the final towers or tourilles of the condensing system, is also frequently called "tower acid," particularly when used to supply the Glover tower of a chamber system. "Aqua fortis" or "strong water" (because of its great solvent power) is the name given nitric acid by Geber (A.D. 750–800), or one of his immediate predecessors, who made it by heating together saltpeter, copper vitriol and alum. The first mention of the present process of making it is by Basil Valentine (A.D. 1450–1500) who says, however, that this method had long been used. Nitric acid was, therefore, one of the earliest mineral acids known.

Industrial Importance. Nitric acid occupies a peculiar position, somewhat like that of sulphuric, of great industrial importance as an intermediate step in the production of other products. Its salts are used to some extent in electroplating since practically every one is soluble, in fireworks and colored lights because of their high oxidizing power, and it is essential to the manufacture of many organic compounds besides nitrocelluloses, azo and diazo dyes. In tonnage and value, it stands among the leading chemical products, the yearly output being 54,190 tons, valued at $5,232,527. In the form of nitrates or substitution products it is essential in some way to the production of practically every explosive, 181,874 a very large proportion of the synthetic dyestuffs, azo, diazo and

amido, also pyroxyline plastics, while its salts (chiefly from natural deposits), are used for fertilizer in this country to the extent of 43,373 tons. The growth in the manufacture of these products is shown in the following table:

	1900	1905
Nitric acid:		
Quantity, tons........	31,542	54,190
Value................	$2,964,700	$5,232,527
Fertilizers:		
Quantity, tons........	2,887,004	3,591,771
Value................	$42,097,673	$56,973,634
Explosives:		
Quantity, tons.......	109,136	181,874
Value................	$16,552,011	$28,204,517
Synthetic dyestuffs:		
Quantity, tons........	3,849	5,320
Value................	$2,280,899	$2,665,134
Pyroxyline plastics:		
Quantity, tons........	1,037	1,483
Value................	$2,259,338	$2,671,380

Nitric acid, particularly when strong and pure, approaches the value of a fine chemical, costing from 4 to 5½ cents per pound of the HNO_3 it contains, and selling from 5 to 7 cents. Much less " weak acid " is made and sold than formerly for two reasons. First, the improvement in nitric acid processes has made it possible to produce all the acid of sufficient strength for " bleaching " (i.e., removing red lower oxides of nitrogen) if not already bleached in making. Second, the development of the sulphuric contact process making 105 per cent H_2SO_4 has made the entire output of the nitric acid plant (average 87–88 per cent) available for making mixed acid. When the sulphuric economically obtainable was only 98 per cent, it was necessary to use 93 per cent HNO_3 for making mixed acid for nitroglycerine, dynamite, guncotton, etc., and only about one-half to three-quarters of the output of a nitric plant was strong enough for making " mixed acid." The balance had to find a market as weaker acid or as nitrates.

Properties. Strong nitric acid when free from lower oxides and freshly made is practically colorless, but the action of light, slightly elevated temperatures, or traces of organic matter, generally gives it a slight pale amber tint gradually developing into a clear pale red-brown. It is more mobile than sulphuric acid of like strength and about one-third lighter in weight. Pure acid of 99.5 per cent reaches a specific gravity of 1.52 (49.6° Bé). Unlike sulphuric acid, the anhydride is not stable in solution in the acid (unless H_2SO_4 is present), so strengths higher than 100 per cent are not made, but N_2O_4 dissolved in the acid increases its specific

gravity until 12 per cent of N_2O_4 has a density of 1.62 (about 56° Bé.), and shows a greater oxidizing power than the pure acid.

The destructive action of nitric acid on organic matter is rapid, partly oxidizing and partly nitrating (forming nitric esters or NO_2 substitutions). The oxygen containing bodies of the paraffine series tend to form oxalic acid, the —CHOH groups to form esters, a characteristic also exhibited by cellulose, glycerine and under proper conditions, starch. The sulphur-containing bodies tend to sulphonic acids, while the aromatic series is characterized by its greater tendency to form nitro derivatives. Most ordinary metals are attacked by nitric acid of various strengths, gold and platinum excepted. The hydrogen liberated acts upon the nitric acid to reduce an additional portion of it, liberating various oxides of nitrogen, depending on the concentration of the acid and the temperature. Broadly speaking the more concentrated the acid the more higher oxides will be produced and dilute acid will be largely reduced to ammonia. Lead and iron, however, are somewhat slowly acted upon by strong acid, iron in particular being the material generally used for the distilling parts of nitric acid apparatus. Its protection at this point is due to three causes, chiefly the presence of sulphuric acid, superseding or inhibiting the action of the nitric and forming insoluble sulphates which protect the surface; second, the high temperature which prevents condensation of acid on the surface, and lastly to some extent the peculiar passivizing action which nitric acid possesses for iron surfaces.

Manufacture. In this country Carter & Scattergood of Philadelphia, began the manufacture of nitric acid in 1824 but the industry was not very important until 1862, when the discovery of nitroglycerine, followed by other nitro-explosives, opened a new field for it.

Two general methods of making nitric acid are important, first, the old reaction of Basil Valentine from nitrate of soda (natural deposits) by action of an excess of sulphuric acid and distillation of the liberated nitric acid, the reaction approximating,

$$NaNO_3+H_2SO_4=NaHSO_4+HNO_3.$$

The presence of chlorides in the nitrate liberates HCl which reacts,

$$HCl+HNO_3=H_2O+NO_2Cl,$$

each atom of Cl carrying away an atom of N which is lost to nitric acid manufacture. Too high a temperature at the start increases a side-reaction, always present to some extent particularly in the presence of a dehydrating agent like an excess of sulphuric acid; i. e.

$$4HNO_3=2H_2O+O_2+2N_2O_4$$

The N_2O_4 thus produced is difficult to condense and injurious to the product. Too high a temperature at the end of the distillation

tends to the formation of sodium pyrosulphate and water according to reaction

$$2NaHSO_4 + heat = Na_2S_2O_7 + H_2O$$

and further,

$$Na_2S_2O_7 + heat = Na_2SO_4 + SO_3.$$

The volatile products of both of these reactions are injurious to the strength and purity of the nitric acid produced.

The second method is synthetic and developed from Sir Wm. Crookes' fascinating suggestion in 1890, that the ultimate exhaustion of the natural deposits should be anticipated by perfecting the combustion of air, giving a practically inexhaustible source of nitrogen products for fertilizers. This modern process consists in burning the nitrogen of the air with its oxygen in an elongated electric arc and quickly cooling the resulting gases. It is only within the last five years that it has developed commercially—principally in Norway, Sweden and Switzerland because of the cheap water power available there. Mixed oxides of nitrogen are thus produced and their oxidation completed in reaction towers after which they are absorbed in milk of lime. The acid neutralized produces "nitro-lime" chiefly used for fertilizer. It is questionable whether the production of strong nitric by this process can be carried out economically except when extremely cheap electric power (from water falls) is available. In this country one commercial failure was made during the early stages of the development of this process, but another installation is practically completed and under much more favorable auspices promises better results. As a method of making strong nitric acid however, it offers little inducement. Weak nitric acid increases in strength on distillation until 69 per cent is reached, after which a hydrate ($2HNO_3 \cdot 3H_2O$) of about 70 per cent HNO_3 distills over at a constant boiling-point. Some methods of overcoming this difficulty and making the synthetic process directly available for the production of strong acid, have been proposed but commercial success has not yet been attained.

The practical processes, then, make nitric by treatment of sodium nitrate with sulphuric acid. Four methods of decomposing have been claimed as successful, those of Prentice, Uebel, Valentiner and the various forms of plain still (most generally used in this country).

Prentice Process. This method consists in continuously mixing the nitrate and an unusually large excess of sulphuric in a separate vessel provided with a condenser to which the N_2O_4 and Cl liberated are supposed to pass, leaving the nitric to be distilled off free from these impurities. It was said to have worked for some time satisfactorily at Stowmarket, England, and to be capable of producing its entire output at a strength of 94 per cent. The feature apparently most criticised was that 12 parts of oil of vitriol were required for 10 of nitrate of soda, but this is

no more than should be used to get a good niter cake containing 30 per cent free acid, easy to fuse and fluently mixing. A very slight loss of nitric at 4½ cents per pound, quickly makes up for any saving in sulphuric at half a cent per pound. The acid then made was not what we would regard as well bleached but this could easily have been remedied.

Uebel's Process. In this system Fig. 146, half of the niter cake (approximately $NaHSO_4$, which results after expelling the last nitric acid from a charge in retort *A*), is run into an equivalent weight of moderately strong sulphuric acid in the pan *B* located over the flue *C*. In this pan the

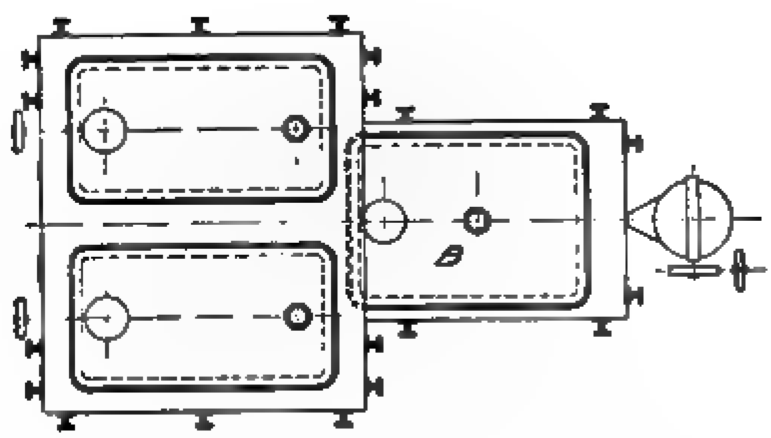

FIG. 146.

heat of the niter cake serves to drive out 15 or 20 per cent of water from the sulphuric acid, and form practically anhydrous "polysulphate" $NaH_3(SO_4)_2$. This is maintained in a fused condition by the heat of the flue *C* below, retained by the cover *D*, and is drawn off by the valved pipe *E* and the gutter *F* into a hoisting pot *G* that can be elevated by chain fall or power hoist and by trolley rail carried over the feed hole of the retort *H* or *H'*. These are charged alternately, at intervals of about 4 hours, with 700 to 900 lbs. of nitrate of soda, dried by spreading out in the iron pans *J*. Charging is done through the feed hole *K*, which is then closed with a stone or stoneware plate *L* and covered with nitrate of soda. Sometimes the hoisting pot is provided with a bottom nipple (fitting a small hole in the plate *L*) closed inside with a plug valve.

Sometimes the fused "polysulphate" is poured in. Particularly in the latter case it must be added slowly as the hot liquid liberates considerable nitric acid as vapor. To avoid unnecessary heating at this stage the damper *M* is closed, all the fire being given to the retort *H'*, which is then being boiled off. When the polysulphate is all in (about 45 minutes) the damper *M* is opened and the boiling off of *H* is begun, which occupies from 2 to 3 hours. During this time boiling off of *H'* is completed, the damper *M'* is closed and by opening the valve *O* the liquid bisulphate in *H'* is run down to the lower retort *A*. The retort *A* is never wholly emptied (except in shutting down) so that the incoming bisulphate blends with the already highly heated charge and thus gives up the last of its nitric acid. The now empty retort *H'* is then (usually after slight cooling) charged with its nitrate of soda and a fresh hoisting pot of liquid polysulphate. As a matter of fact, however, Uebel's retorts are generally operated with sulphuric instead of polysulphates.

Valentiner Process. By this method the nitrate is decomposed under a vacuum. At first the suction was commenced as soon as the charge was made and increased until about one-third of an atmosphere remained, when the heat was applied. It was found, however, that the intimate mixture of nitrate and acid was better insured, and frothing which carried suspended nitrate upon the sides of the retort, was prevented by throttling the outlet of the gases. About 2200 lbs. of nitrate is charged into the retort *A*, Fig. 147, through the hole *B* having an iron lid, which is then carefully luted. Sulphuric acid (2360 lbs. 66° o.v. or preferably 96 per cent) is then run in from a measuring tank or scale tank *C* by a pipe *D* goosenecked and provided with a cock. When the acid is all in, suction is applied by means of the 12×16 inch, 60 r.p.m. vacuum pump *E*. This is protected from the acid fumes and chlorine liberated from any NaCl in the niter by a series of wash bottles alternately empty and about half filled with milk of lime. Pipes may be arranged as indicated to insure against either sucking back or absence of liquid in its proper wash bottle when operating. Under the suction and heat of reaction rapid evolution of nitric vapor begins. To prevent its becoming too rapid a throttle plate with a small hole is inserted between the still and the gas pipe *G*, which is provided with a Y-branch for cleaning and is surmounted by a short length of wire-covered glass pipe *H* for observing the color of the passing vapors. A reducer pipe to 2½ ins. then takes the gases to a small tourille *I* filled with broken pumice, where entrained sulphuric or niter dust are separated. Thence the gases pass through two large stoneware coils *J* and *K* (2½ in. bore and about 45 sq.ft. cooling surface), placed in wooden tanks supplied with cold water at the bottoms and provided with overflows near the tops. Here the acid is largely condensed and most of it flows into the large receiver *P*. Wire-covered glass pipes *L* and *M* are provided at the outlet of each coil for observing the color and rate of flow of the acid and a device *N* for

drawing samples for testing. A three-way cock *O* is provided to pass any weak or discolored acid into the smaller jar *S*, the flow to which can be observed at *R*. Any air or uncondensed vapor from the coils passes through the pipe *Q* and the jars *S* and *T*, where it deposits some acid, and then upward through the reflux cooling worm *V*, 2½ in. bore about 22 sq.ft. cooling surface, where nearly all the condensable vapor is caught and returned to the jar *T*. Weaker acid collected in *S* and *T* may be added to the 96 per cent or 98 per cent sulphuric used for charging the retort. Bleaching of the acid is not required in this process for two reasons: the solution pressure of N_2O_4 and Cl in the acid is greatly reduced by the vacuum, and also the low temperature of vacuum distillation causes very little breaking up of the nitric to form N_2O_4. The slight loss corresponding to the HCl liberated and oxidized to nitrosyl

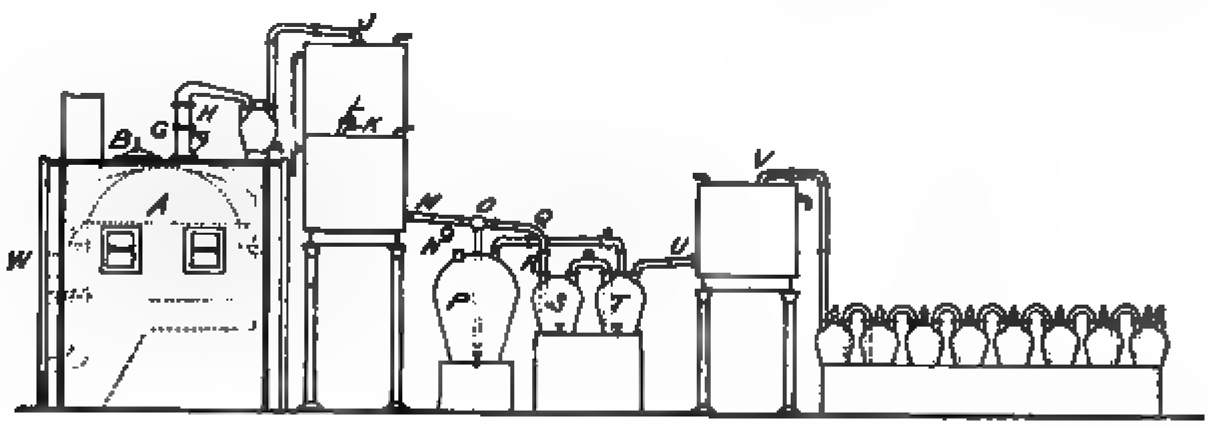

FIG. 147.

chloride at the expense of nitric is inevitable. No loss by leakage of joints can occur under suction and less breakage of stoneware results from the lower temperatures employed. More continuous rapid evolution of vapor makes it possible to run off the charges in about eight-hour cycles. After the first application of two-thirds of an atmosphere suction it gradually increases as evolution of vapor begins to reduce the temperature in the retort. Heat is then gently applied until the retort reaches 80° and, as the rate of vapor evolution again decreases, is gradually raised to 130°. When the acid flow ceases the pump is shut off and the heat raised to facilitate running of the niter cake through the bottom spout *W*. An excellent quality of acid (N_2O_3 = .05 per cent) is produced, about 80 per cent averaging 96 per cent HNO_3, or the whole output averaging 89 per cent if weak acid is returned with the sulphuric to the retort. The niter cake produced is of excellent quality. The statements found in the literature that "perfectly pure nitric monohydrate (HNO_3) produced by this process, is now found in commerce" is however an exag-

geration, although the writer regards the process as one of the best on the market to-day.

Common Process. By far the greater proportion of nitric acid, however, is made by the simple action of sulphuric acid on the nitrate of soda at substantially atmospheric pressure. This reaction is generally carried out in ordinary cast-iron retorts either of cylindrical pattern horizontally placed, or of the general shape of deep pots. The former is illustrated in Fig. 148

Fig. 148.

in which *A* is the brick setting properly provided with buckstays *B*. Through this setting extend cast-iron cylinders *C* provided at either end with a closing plate *D* consisting of either cut stone or cast iron. One of these plates, generally the one above the firing door, is provided with two holes. The smaller hole *E* serves for the introduction of the acid and the larger hole *F* for the charging with nitrate of soda, after which it is closed either by a luted cover or by a screw plate. The plate on the opposite end is provided with holes *G* into which the exit pipe for gases is luted and *H* for tapping off niter cake. These cylinders vary from 3 ft. in diameter, 5 ft. in length, to 5 ft. in diameter and 10 ft. in length, sometimes the diameter being as great as 5 ft. 6 ins. The charges of nitrate of soda are 700 to 2200 lbs. It will be noted that a relatively small grate area and a single fire is used and much of the success of the operation in yield, quality and speed depends on its careful manipulation. According to the older practice only a slight excess of sulphuric acid was used and the niter cake remaining behind was consequently so hard that it was necessary to get into the still and dig it out. Modern practice, which to a very large extent utilizes the niter cake for other manufacture, permits 33 to 36 per cent excess of sulphuric to remain in the niter cake. The end plate, generally that in the rear, is provided with a hole at the bottom for withdrawing the niter cake, this hole generally being closed by an iron peg or tap loosely ground in and sometimes held in place by a screw handle.

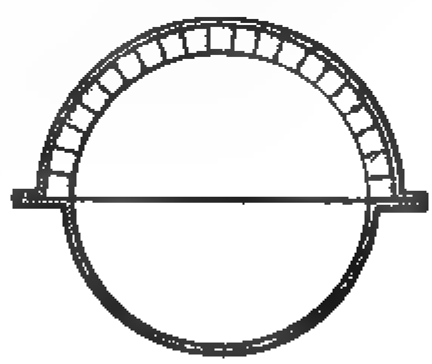

Fig. 149.

One development of this older form of still is indicated in Fig. 149,

which shows the still in section, the lower half being given a somewhat wider flange, the upper half being of larger diameter and lined with brick to protect this half of the still from the action of the nitric gases. In some plants the nitric stills are cast all in one piece with the necessary manhole at one end and the inlet and outlet pipes for acid and gas located on the axis of the cylinder. Some prefer to have axial trunnions (bearings in the brickwork) cast on the ends and an opening on one side of the cylinder to be turned upward during charging, thus permitting the cylinder to be rotated on its axis when the niter cake is to be removed, dumping the same in a pocket to the rear of the fire-bed. Considering the fluidity of the niter cake, however, there seems to be little object in this mechanical complication.

FIG. 150.

Pot Still. Another form of still, pot-shaped in general outline, is shown in Fig. 150. The bottom, middle section and cover being cast in separate pieces to permit of separate renewal according to the wear which they have suffered. The belt and top are generally lined with brick as indicated in Fig. 151. The bottom piece is left unlined to permit the free transmission of heat and because the corrosion at this point, where there is always plenty of sulphuric, is very much less. The bottom of this pot is pro-

FIG. 151.

vided with a hole *F* set in a trough *G*, thus permitting the bisulphate, when the charge is completed, to be run out into a pan or wagon. The gas outlet *H*, 3 to 6 ins. in diameter, and the charging hole *I*, 8 to 10 ins. diameter are provided in the cover. These sections are luted together with acid-proof cement, for which purpose "Vitrex" cement may

well be used; or cement made up at the works from asbestos powder containing a little finely powdered barium sulphate, made into a thick paste with 5 per cent silicate of soda solution; or equal parts iron filings and powdered brimstone, thoroughly mixed with 4 parts of ground firebrick with as little water as will serve to make a thick putty.

Charging. After completing one charge and before putting in another, the retorts are allowed to cool somewhat as the hottest part of the operation is at the end, which temperature would be too high for initiating a new charge. The nitrate of soda charge is then dumped into the still, generally after drying if strong acid is required. The manhole plate is luted or clamped on and the sulphuric acid run in rapidly. Evolution of nitric begins before all the sulphuric acid has been added, but a light fire is started before the evolution slackens and the heat is gradually increased so as to ensure a steady flow of nitric acid. A single charge of 2200 lbs. is generally run off in one of these large-size retorts in 24 hours, though by skillful manipulation it is possible to secure two charges in 24 hours or at most, 27 hours. In many factories, however, it is found most satisfactory to have the still started in the morning, under the eye of the superintendent, and have no charging done at night.

Distillation. The first run of the acid is generally weak, or impure or both. It is the writer's experience that to some extent this depends on the character of nitrate used and the strength of the sulphuric acid applied. Nitrates containing chloride will produce impure acid to begin with because of its contamination with nitrosylchloride. If the charges are made in too hot a still or if the sulphuric acid is run in too rapidly, there will be considerable lower oxides in the first run of acid. Likewise, if impure nitric, recovered from the final towers of the condensation system, has been mixed with the sulphuric used for charging, most of its impurities will come over in the early stages of the reaction. The retort should not be too cold at the time of charging or the partial condensation of nitric acid on its surface will cause excessive corrosion with contamination of niter cake and early destruction of the still. The whole retort should be as nearly as possible the same temperature throughout; therefore it is desirable to have the retort enclosed as completely as possible in the brickwork. This temperature should be very slightly above the boiling-point of the nitric acid, enough above, however, to materially warm up the charge of niter when added. The nitrate of soda is preferably dried and sulphuric acid used at approximately 93 to 95 per cent, or equivalent strength of H_2SO_4 after diluting with recovered nitric. Too strong sulphuric is apt to promote the formation of lower oxides by dehydration of the nitric acid. Too early an application of the fire or too rapid introduction of the sulphuric, or too high a temperature of the still are all apt to produce irregular and incomplete mixing of the charge by distilling out too much nitric in the initial stage of the operation. When all conditions are right, a gradual and steady distillation should begin when about

one-third of the sulphuric acid has been introduced and should only reach its full strength just after the last of the sulphuric has been added.

Condensation. There are two general methods of carrying out the condensation of nitric acid. In the older method the condensed acid brings down with it such lower oxides and chlorine as it may carry and the product is separated into stronger or weaker fractions according to the requirements of the market and the uses to which it is to be put in the plant. This system is naturally best adapted to the production of extremely high strength acid, because of the separation of various fractions. It is necessary, however, to treat the acid thus produced in order to purify it. This is done by heating the acid and blowing out the impurities with dry air. Some of the high strength secured is lost because of the tendency of the strong nitric to distill out of the mixture. The other method consists in treating the distillates from the still on the reflux condenser principle and making the heated gases, sometimes mixed with a little air, coming from the still serve the purpose of bleaching the acid, thereby producing substantially the entire output of the still at a somewhat lower percentage, but all of highly bleached and purified quality so far as lower oxides and chlorine are concerned. Other systems of condensation combine, to a greater or less degree, the two different characteristics above outlined. Three or four such systems will be described; in the first instance to show the extreme of condensation and subsequent purification and in the last to show the extreme of complete production and automatic bleaching by the action of the hot gases.

Fig. 152 illustrates the condensing plant designed to operate under the first mentioned systems, i.e., collection and subsequent purification of the acid. The distillate from still *A* passes over into a first receiver *B* designed to catch any impurities carried over by foaming or excessive violence of distillation. The acid in this receiver is, however, under normal conditions, clear and pure enough for use along with the major portion of the production. Provision is therefore made for carrying this acid down by the pipes *C* and the gutters *D* to the general receiving reservoir after it has been examined and proved satisfactory for use. The greater portion of the gas, however, passes up through the pipe *F* and is condensed in coils *G* surrounded by water in a wooden tank, whence the condensed acid flows along with the uncondensed remainder of gas into the receivers *H*. Herein collects the greater portion of the condensed acid and it is not unusual to provide a pair of receivers in the position *H*, one intended for strong and the other for weak acid. In the pipe between *G* and *H* is provided a three-way cock so that the acid according to its strength may be separated into one or other of the receivers. Two reservoirs *E* are provided for receiving the acid respectively from the two receivers *H*, whether it be strong or weak. After leaving the receiver *H* the gases pass over into a second receiver *I* wherein the residual portion of suspended liquid may be collected, as also the return drips from the gas pipes leading

into the recovery towers *K* and *L*. This gas line is provided with branches *J'* to bring the gases from the receiving tank *M* into which strong acid is blown from the receiver *E* when it is desired to bleach the acid; also the branch *J''* from the receiver *E* to carry off any unoxidized gases that may be generated in that receiver and the branch *J'''* from the receiver at the top of the tower into which the stronger spraying acid is blown. The two towers *K* and *L* are connected in series, packed with coke and provided with an outlet *N* connected with a chimney or other source of draft. In these towers the lower oxides of nitrogen are absorbed in respectively stronger nitric in the tower *K* and water in the tower *L* and oxidized by the air which comes through the system along with these

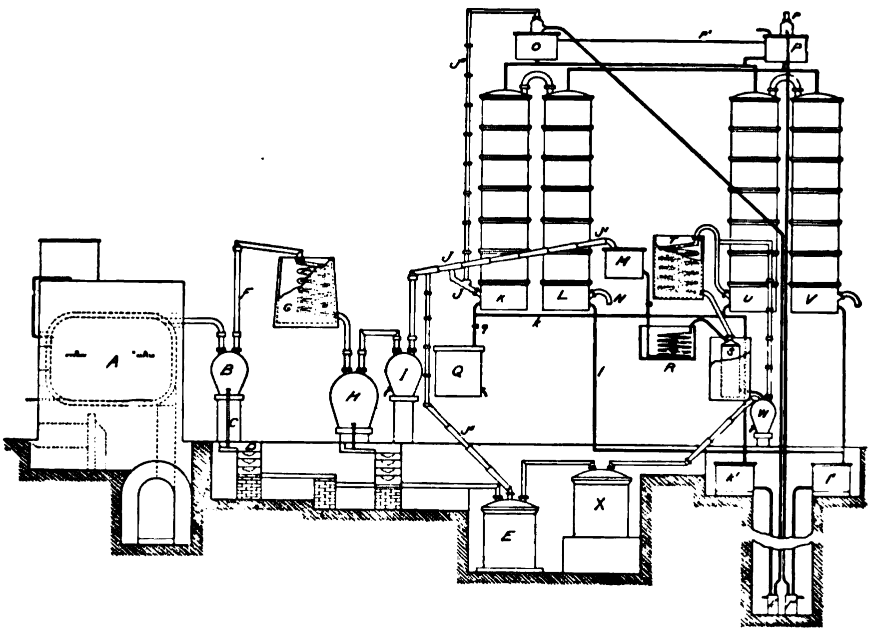

FIG. 152.

gases from various leakages, etc. The weak liquid going down the tower *L* passes through the pipe *l* into the receiver *l'* whence it goes into an air lift *l''* and is thrown up thereby into the storage tank *P* at the top of the other set of towers. From here a pipe *p* permits the exit of the air used in blowing to the atmosphere because the acid in this tower is so weak that little gas will be carried away from it. From the tank *P* a pipe returns the weak acid to the top of the tower *L* which contains a distributor to insure equal flow of acid down through the cross-section of the tower. The receiver *L'* receives a slight but steady flow of water maintaining the acid in the system of the tower *L* at about 18° to 20° Bé. Naturally with the addition of water absorption of gas and oxidizing of this gas into nitric acid, an excess of acid accumulates in the tank *P*.

This excess is permitted to overflow by gravity to the pipe p' into the strong acid receiver O, from the bottom of which a supply pipe is carried to the tower K. From the bottom of this tower K a pipe k carries the strong tower acid into the receiver k' whence it passes into the air-lift k'' and is elevated into the receiver O. In this tower the stronger gas is absorbed and oxidized and a portion of the outflow from the tower K is permitted to pass out through the valve q into the receiver Q for the recovered tower acid which will be from 35° to 40° Bé. The strong acid accumulated in the receiver E is elevated by a Montejus or air lift, not shown, into the receiver M, which is the acid supply reservoir for the bleaching system. From here it is allowed to flow in a slow stream through the coil R immersed in a hot water tank and thence into the tower S, which is likewise immersed in a deeper hot water tank and is filled with pumice stone or coke. The temperature of the hot water in the two tanks is carefully regulated to heat the acid to approximately 80° C. and a slow stream of air is supplied to the bottom of the tower S through pipes not shown. The acid warmed up in the coil R and flowing down over the extended surface of the coke or pumice in the tower S is fully exposed to this stream of warm air and thus oxidized. At the same time whatever lower oxides of lower oxides of nitrogen not thus oxidized are blown out by the stream of air and with it into the coil above.

This coil is connected as a reflux and is given a very small supply of water, since the object is only to condense the liquid which might be carried out with the gas. The lower oxides pass out through the coil T into the strong tower U of a separate recovery system, where they are oxidized as were the lower oxides from the generating plant in the tower K. Likewise a second tower B for weak acid is provided similar to the tower L. The supply of acid for U is taken from the reservoir O which supplies the other strong tower K and the weak acid for supplying the tower V is taken from the reservoir P. The outflow lines at the bottom of the towers U and V respectively, join the lines k and l respectively from the strong and weak recovery towers connected with the generating system and the same air lifts furnish a continuous supply for both the decomposing and the bleaching system. After passing down through the heated tower S the acid is entirely freed from chlorine, contains less than 0.10 per cent lower oxides figured as N_2O_3 and is received in the jar W for test and examination, whence it is run by a pipe not shown into the final receiver for bleached acid X. This system will seem to be somewhat complicated, but it is found to be thoroughly efficient and lends itself readily to careful control to the quality of acid at various points. Some of the larger manufacturers of strong nitric, for use in making mixed acid, both in this country and abroad, use this system, with great success. From 94 to 96 per cent recovery of the nitric from nitrate of soda is made and the average strength of all acid produced returning weak acid from the receiver Q into retort A along with the sulphuric acid used, is about

88 to 89 per cent without special drying of the nitrate of soda and using sulphuric acid of about 98 per cent before dilution with the weak nitric.

Gutmann Condenser. Somewhat similar in principle though less complicated in arrangement is the condenser system of Gutmann illustrated in Fig. 153. Here the gases from the stills *A*, *A′*, etc., are taken over through

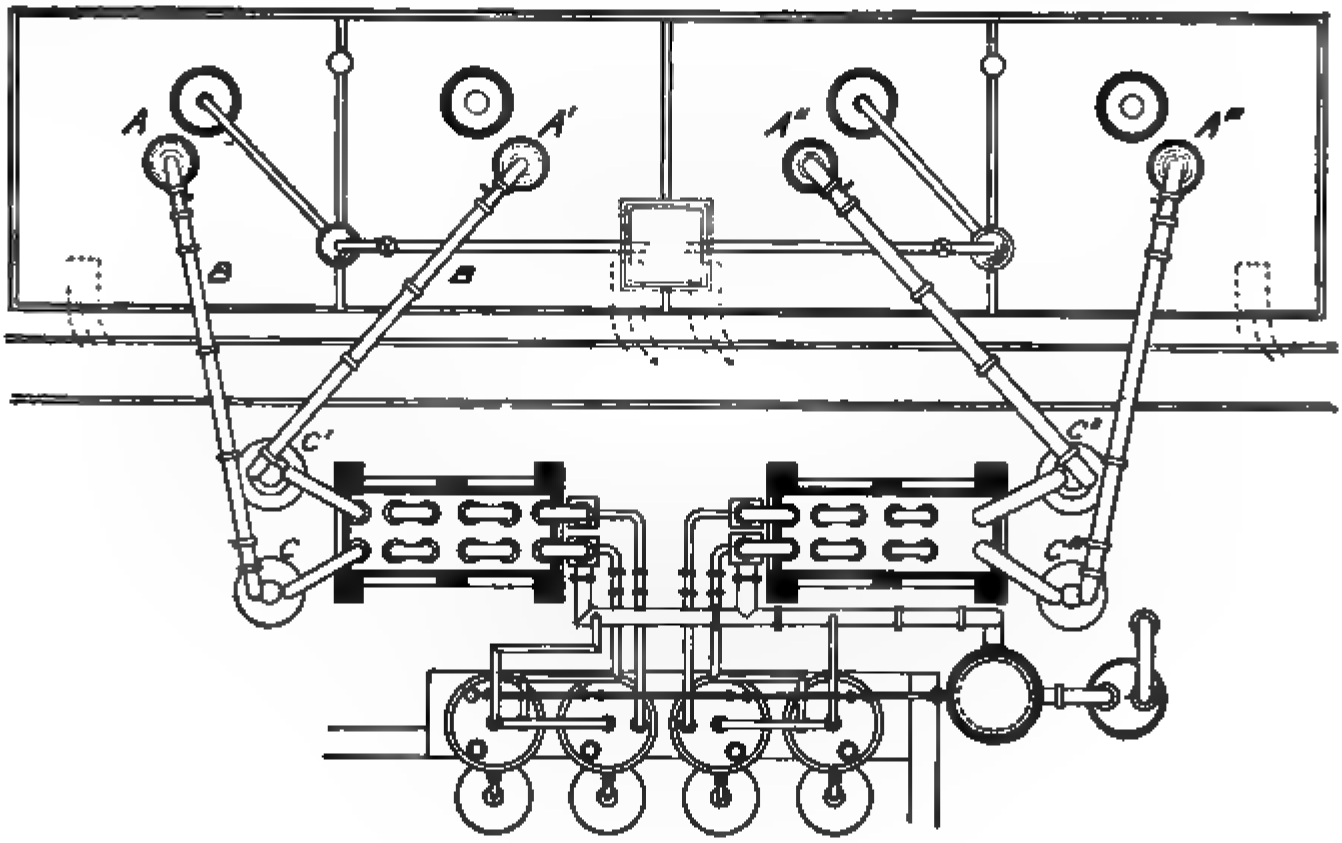

Fig. 153.

Fig. 154.

the long stoneware pipes *B*, to preliminary receivers *C*, *C′*, etc., similar to those used in the plant just described. These serve a similar purpose, i.e., to catch any suspended or entrained matter that may be carried over by foaming or by excessive violence of gas evolution. Fig.

154 shows a side view of the same plant and Fig. 155, an end elevation. As will be seen in the side view the receivers *C* are in this case also connected with the general acid line to the finished acid receivers so that if the acid collected in the receiver *C* proves of satisfactory quality it can be run in with the rest of the production from the plant. From this receiver the gases pass up through the pipe *D* into a series of vertical earthenware pipes set in water in a wooden tank. The joints are made just above the surface of the water and just below the bottom of the tank. The pipes passing out through slightly tapered holes in the bottom being surrounded with heavy rubber rings, stand down into the hole so as to make a water-

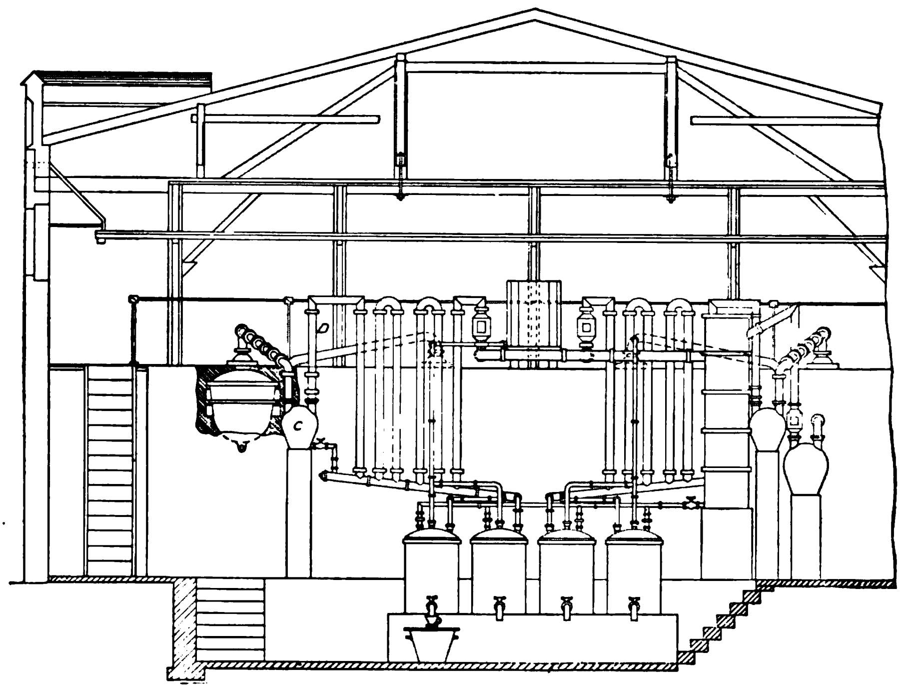

FIG. 155.

tight joint. The water in this tank is maintained slightly warm and by proper manipulation a well bleached acid can be obtained. The gases after passing through these water-cooled pipes unite in a general gas main which conveys them to the final recovery tower, which is sprayed with acid from a receiver, not shown in the drawing, in a manner similar to that described in the previous plant. Here, however, only one tower is customarily used and the weak acid made is not as strong as that obtained in the other installation. Lanterns are provided for observing the color of the gases and controlling in this manner the draft of a chimney connected to the pipe through a final receiver intended to catch any last traces of suspended acid coming over from the splash of the

distributor in the tower. The yield from the Gutmann plant is excellent and substantially all the acid is made in a ready bleached condition, but the securing of this result requires somewhat careful manipulation of the cooling water and where there is no chamber plant to receive the weak acid made in the tower it is desirable to have two towers in series so as to produce the weak acid of somewhat higher strength that can be used to better advantage in mixing with the sulphuric supplied to the retort. An injector is inserted in the gas pipe between the still and the first receiver and supplied with compressed air heated by passing through pipes set in the brickwork. This hot air serves two purposes: First, to quickly draw the gases away from the still and so far as possible shorten their contact with the hot iron, and in the second place it supplies the necessary oxygen to carry on a considerable amount of oxidation of the lower oxides of nitrogen in the pipes *B*, the receiver *C* and the warm condensing pipes immersed in the tanks.

Skoglund Condenser. In most nitric acid plants the aim is to combine the condensation and bleaching into a single step, by doing the condensation at such a temperature that as little of the lower oxides of nitrogen shall be condensed with the acid as possible and that in the second place what little is condensed shall be supplied with sufficient hot air to carry out its oxidation at once and produce in a single step a water-white acid of high strength. The simplest, and in the writer's opinion the most efficient, apparatus for this purpose is the condenser system of Skoglund, see Fig. 156. It is characterized by the carrying out of this preliminary condensation and bleaching action in a tower somewhat similar to, though smaller in size than the final towers used for the oxidatign of lower oxides that cannot be condensed. From the still *A* the gases pass over in the usual manner into a tourille or jar *B* serving as a sort of safety bottle to catch any suspended matter that may be carried over when the still foams. From here they pass through a pipe *C* into a special injector pipe *D* which is arranged to be served with compressed air and thence into the bottom of the tower *F*. This tower is filled with lumps of quartz through which the hot gases mixed with air pass upward, while the acid, after condensation, flows downward. From the top of the tower the gases pass through a condenser which is generally a water-cooled coil. In this figure it is shown as an air-cooled series of pipes *G* which may, however, be water cooled if desired by covering each with a piece of linen and trickling water down upon them from above. The purpose of the linen is to distribute the film of water equally over the surface of the pipes and not permit it to flow through certain lines caused by salt deposits, thus producing irregular cooling and consequent breakage of the pipes. From this condenser the gases pass over by a pipe *F* to the bottom of the tower *H* and thence through the tower *H′*, both of which are similar to the final towers in either of the other systems described, The acid produced in the condenser *G* flows downward through the tower.

entering it at almost the boiling-point, which temperature is maintained throughout its entire flow over the surface of the quartz. Accumulating at the bottom of the tower, the acid then flows out through the pipe *I* into the small jar or tourille *J*, whence it flows through the cooling worm *K*, out of the top of this worm through the overflow *L* and into the final storage jar *M*. Similar storage jars are provided for the acid from the towers *G* and *H* so that it may be returned with the sulphuric acid into the still *A*. Through the center mouthpiece of the jar *J* another hot-air pipe is carried to the bottom of the acid in *J* and the large mouthpiece of *J* is connected with a similar inlet to the tower so that instead of using the injector through the pipe *D* air is preferably blown through the hot

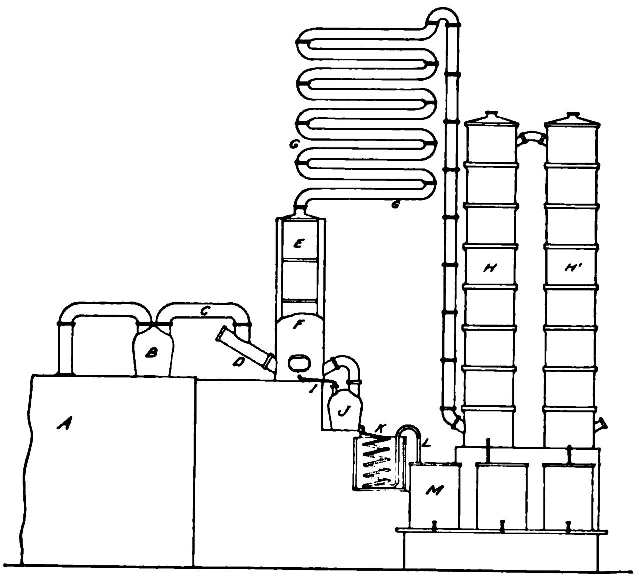

FIG. 156.

acid collected in the jar *J* and the gases thus removed carried back into the tower. In order to maintain this tower at a high temperature it is customary to connect 3 or 4 stills charged in rotation to a single tower. Either the bottom of the tower is provided with inlets on three or four sides, or else a common gas main is employed, into which the injectors *O* are connected. The jar *B* is asbestos covered but it cools down considerably after each charge and serving as a sort of preliminary condenser to catch the first weaker acid that comes over when the still is charged. In some cases this acid is added to the condenser acid at the top of the tower by means of a specially provided neck, but generally it is mixed with the sulphuric acid and the weaker acid from the final towers *H* and *H'*, the whole being returned to the still with the nitrated soda of the succeeding charge. Using moderately dry (not specially dried) nitrate of soda and 98 or 99 per cent sulphuric diluted with the weak nitric acid to a strength

of approximately 93 per cent H_2SO_4; the average output from this plant is from 89 to 90 per cent in strength, perfectly water-white and substantially free from chlorine. The operation is conducted under a slight suction. As the tower *E* is carefully jacketed with insulating material so as to maintain its high temperature and protect it from contact with the cold air, and the pipes *C* and *D* are also carefully jacketed, there is practically no risk of breakage except of the air-cooled pipes *G*. This breakage is as small as can be credited to any form of nitric condensation.

Storage and Packing. Nitric acid is stored in stoneware pots or in the carboys to be shipped. For the manufacture of mixed acid, however, it is most conveniently stored along with a portion of the sulphuric acid with which it is necessary to mix it. When containing 5 per cent of sulphuric acid and not over 3 per cent of water, the mixture may be quite safely stored in iron tanks for an indefinite period. Iron is much preferable to lead for strong acid, while stoneware is better than either for weaker acid. The carboys used for the shipment of nitric acid are usually not packed with hay because of the risk of fire should a carboy be broken and the strong nitric acid come in contact with the organic material. The rubber-packed carboys described under the chapter on sulphuric acid are much preferable for nitric acid.

IX

SALT, HYDROCHLORIC ACID AND SODIUM SULPHATE

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Salt. Common salt has been known and used since the time of the earliest man. It is an important constituent of food for both man and animals. It is found in all parts of the world. Small amounts are present in most river waters and some spring waters are impregnated with large quantities of it. Sea water contains it to the extent of about 3 per cent, while the water of the Dead Sea contains about 10 per cent and that of the Great Salt Lake, 9.7 per cent. It is also found in large deposits as rock salt, where it may exist in a colorless transparent form or with varying grades of purity down to a marl-like mass which contains but little salt. The deposits that are worked usually consist of salt not in transparent condition, but in a white, gray or red massive state. When it is transparent it will split out in cubes, but there is no cleavage in its more impure conditions. There are many deposits of rock salt in Germany and Austria, the most important being at Strassfurt. In Spain there is a bed of importance; and in fact all countries possess some salt deposits. In the United States the most salt is produced in Michigan. From these deposits, in 1907, 10,786,630 barrels were produced, valued at $2,062,357. New York furnishes less, but it is of better quality. Ohio, Virginia, Utah, and Louisiana, also, have salt deposits of considerable extent. Rock salt and brine, with few exceptions, contain so much impurity that for the table and for many manufacturing purposes the salt must be purified before use.

Properties. Sodium chloride is a colorless, crystalline solid, with a specific gravity of 2.13, crystallizing in cubes often with hollow faces. It melts at 815° C. or 1500° F., and volatilizes below a white heat. There is little difference in the solubility of salt in hot and cold water, 100 parts of water at 0° dissolving 36 parts of salt, while 100 parts of water at boiling temperature dissolve 39 parts. This fact makes it possible to separate salt from its impurities, as most other substances are much more soluble in hot than in cold water. Absolutely pure salt is not hygroscopic, but ordinary salt will attract moisture from the air, sometimes in quantities sufficient to

form a paste. This is due to the presence of admixed calcium or magnesium chloride, which always accompanies salt in its deposits.

Theory of Deposits. The salt beds always give indications of being the result of the drying up of salt seas. In these deposits the admixed salts are found in the relative order of their solubility. On the bottom are found the insoluble calcium sulphate, calcium and magnesium carbonates, while on the top are the deliquescent chlorides of calcium and magnesium, with the chlorides of sodium and potassium and their sulphates and the sulphate of magnesium intermediate in the order of their solubility. The problem of producing commercial salt is to separate it from its impurities, and this is done usually by recrystallization.

Working of Deposit. The working of the salt deposits is dependent upon the purity. In the German deposits and in many others the rock salt is mined, while in other deposits, as in New York, the location of the bed or the large quantity of admixed clay or earthy matter renders this method impractical, and the salt is removed from the ground by boring wells and dissolving the salt out with water. In this case it is important to protect the upper part of the wells with pipes to prevent the absorption of the brine by the surface soil. The brine, whether natural (sea water, spring water) or artificial, must now be concentrated. This may be done either by natural evaporation through the aid of the sun or by the use of fuel. A means of purifying both rock salt and brine in one process consists in saturating the latter with the former and then crystallizing. In warm countries, as along the shores of the Mediterranean, the sea water is collected in reservoirs and then exposed in shallow trenches to the heat of the sun, the salt being removed as it crystallizes, placed in heaps and allowed to drain and dry. This is so impure that it must be refined before it can be used for table or dairy purposes. A process similar to this is practised in working the salt in Great Salt Lake. The water is pumped into crystallizing ponds, which are simply large areas, enclosed with mud banks and divided into smaller basins. The total area of these ponds is about two square miles. The crystallization is carried on from March 15th to September 15th, after which time the liquid is run back into the lake and the "crop" gathered. The "crop" consists of a layer of about 6 ins. of salt, or about 900 tons per acre. The brine which was run back into the lake carries with it the bulk of the impurities, particularly the calcium and magnesium salts, but the gathered salt is largely contaminated with sodium sulphate. This impurity is removed by drying, when the sulphate will effloresce and be reduced to a fine powder. When this powder is acted upon by a current of compressed air the fine sulphate will be blown away, leaving the coarser salt. When this is ground and screened it contains about 98 per cent of sodium chloride. The fine material which was blown out contains about 75 per cent of salt; this is pressed in cakes, and is used for cattle and sheep. This salt is not very satisfactory for dairy purposes, owing to the sulphates which it still contains. In Norway, and other cold countries, the sea

water is concentrated by freezing the water in enclosed basins, then pumping out the still liquid part, which contains all of the salt, and evaporating to crystallization.

Evaporation of Brine. The usual form of apparatus for evaporating the brine by artificial heat is a long, narrow, shallow pan, heated at one end and with flues running the entire length. These pans vary from 40 ft. to over 100 ft. in length, and from 10 to 25 ft. in width. The salt is raked out as it forms. The most difficult impurity to remove here is calcium sulphate, which collects in the form of a scale on the pan. This must be removed, or local superheating will result in the destruction of the pan. Various attempts have been made to use the vacuum pan in the salt-boiling industry, but on account of the separation of anhydrous calcium sulphate, this process has not proven successful. In the boiling of salt, if a small quantity of fat or oil is added to the pan it prevents the formation of a crust on the surface, which would retard evaporation. The salt which is *fished* out of the pans is exposed to steam. This dissolves out the more soluble chlorides of calcium and magnesium, after which it is *whizzed* and dried.

Uses of Salt. In addition to its use for table and dairy purposes, sodium chloride is used in preparing sodium sulphate, sodium carbonate, and indirectly for the production of all sodium salts. It is used in tanning, wet extracting of copper and silver from ores, as a glaze for the common earthenware or stoneware, and as a food preservative. Hydrochloric acid is also produced from common salt.

Some countries impose a tax on salt used for table or dairy purposes; commercial salt being prepared under government supervision and "denatured" by the addition of various substances which would render it unfit for table use, such as Glauber's salt, soda ash, 4-15 per cent, soda crystals, 12 per cent, sulphuric acid, 2 per cent, strong hydrochloric acid, 2 per cent, ammonia liquor, or aniline dye. The use to which the salt is to be put determines which of the denaturing substances is to be used.

Sodium Sulphate. Sodium sulphate occurs in nature both in crystallized form and dissolved in water. Large deposits are found in Arizona, Spain, Peru, Hungary, Siberia, and Hawaiian Islands. Much of this sulphate is pure enough for technical uses. Nearly all natural sulphate, however, contains enough iron to make it unfit for glass manufacture. As a usual thing sodium sulphate is prepared in the anhydrous state, and only a small proportion is converted into the crystallized form.

The usual method of preparing salt cake is by the action of sulphuric acid upon salt, producing hydrochloric acid as a byproduct. In this country, where the Leblanc soda process is not used, hydrochloric acid is made, and the sulphate obtained as a byproduct.

In the manufacture of nitric acid, by the action of sulphuric acid upon soda nitre, the sulphate formed is $NaHSO_4$, which is of very little technical use. In most places this is considered a true waste product, and treated as such. If vitriol and nitre were taken in the proportion required to pro-

duce a neutral sulphate, the extra cost of working and the loss by decomposition would more than balance the value of the sulphate formed. In England it is customary to mix the nitre cake with the salt in the salt cake furnace and work it up in that way. This is seldom done in this country. Many other methods have been proposed for making sulphate, but the only one to meet with success is that of Hargreaves and Robinson, which is used to some extent in Europe, and finds in this country limited application, due largely to the fact that Leblanc soda is not made here. This method consists in passing sulphur dioxide (burner gas) oxygen (air) and steam over salt, when decomposition takes place:

$$2NaCl+SO_2+O+H_2O=Na_2SO_4+2HCl.$$

The salt must be specially prepared, so as to make it porous and thus easily penetrated by the gases. This is done first by grinding the salt, then mixing with water, moulding into a cake and drying between plates. The decomposition takes place in cast-iron cylinders arranged in a battery of eight, six of which are in use while the other two are being recharged. The principle of the counter currents is used here, the fresh salt being acted upon by the gas almost exhausted and the fresh gas coming in contact with the almost converted sulphate. A temperature of 400° must be maintained. The yield is from 93 per cent to 98 per cent.

By far the most important method for the production of sulphate is the old method of decomposing salt with sulphuric acid. This decomposition takes place in two stages: first, $NaCl+H_2SO_4=NaHSO_4+HCl$; second, $NaCl+NaHSO_4=Na_2SO_4+HCl$. The first of these takes place at ordinary temperature, but the second requires considerable heat. The actual decomposition is usually accomplished in two parts of the furnace, except where the cylinder furnaces are used. Here the operation is complete in the one apparatus. The salt and sulphuric acid are mixed in a cast-iron pan and gently heated, usually by waste heat, until the mass becomes stiff. It is then pushed over onto the bed of a reverberatory furnace, where it is heated until all the acid is driven off. In many works, instead of the reverberatory furnace a muffle is used, thus keeping the acid vapors and the furnace gas separate, and not contaminating the sulphate with the furnace dust, thus permitting the use of coal instead of coke for fuel. During the second heating the mass is worked by rakes and slice bars in order to insure complete action.

Formerly the pans were made of lead, but they have almost entirely been replaced by cast-iron pans. The lead pans are still used in making salt cake for the plate-glass industry. The iron pans are circular in shape, from 10 to 14 ft. in diameter, and about 2 ft. deep. They are at the bottom 5 to 7 ins. thick and on the sides 2 to 3 ins. They are built in the furnace and covered with a gas-tight dome made of firebrick, and provided with an earthenware pipe to carry away the hydrochloric acid. Mechanical salt-cake furnaces have been introduced in England, but they

are objected to on account of the introduction of a considerable quantity of iron into the salt cake. These furnaces consist of flat-bottomed iron pans, provided with a shaft carrying plows to keep the mass thoroughly worked up. When the reaction is complete the salt cake is raked out and allowed to cool.

Salt cake contains from 93 per cent to 99 per cent of Na_2SO_4.

The varying quantities of impurities in salt cake, such as $NaHSO_4$, $CaSO_4$, $FeSO_4$, Fe_2O_3, $MgSO_4$, SiO_2, NaCl, depend upon the salt used and the kind of furnace. The sulphate from Hargreaves' process gives a purer product, excepting its content of NaCl, which is high.

Glauber's Salt. In the production of Glauber's salt, the salt cake is dissolved in hot water, filter pressed and run into coolers. If the salt is desired in large crystals (to adulterate crystal soda) the coolers are made of heavy planking and so protected that the crystallization takes place without any agitation. If from 10 to 12 per cent of soda is added with the salt cake, the crystals will be larger, firmer, and more like soda. If small granular crystals are desired the hot liquid is run into large coolers, and when the temperature has fallen to about 30° C. the liquid agitated either by a wooden paddle or by blowing compressed air through the liquid. This gives the sulphate in the form of fine needles, much resembling Epsom's salt, and it was formerly used to adulterate and even as a substitute for that salt. The addition of some soda ash before crystallization serves the double purpose of improving the appearance of the crystals and precipitating the iron. A little milk of lime is also added to free it from iron adulteration.

In order to get a very pure Glauber's salt, the crystals first obtained are freed from the mother liquor by *whizzing*, and are recrystallized. The crystallizing of a batch of sulphate crystals takes from five to eight days in winter, and from fifteen to twenty days in the summer. The great change in the solubility, due to a slight change in temperature, makes it more profitable to push the crystallization during the winter and store up the material during the summer.

The principal uses of sodium sulphate are soda making, glass making, especially window and bottle glass, and for making ultramarine. In the form of Glauber's salt it is used as a mordant, in the production of thiosulphate, in medicine, especially for veterinary uses, and in the making of cooling mixtures.

Hydrochloric Acid. Hydrochloric acid occurs in nature as a constituent of volcanic gases, and is also found dissolved in water. Some of the head streams of the Amazon and other South American rivers have small quantities, but with no commercial value. In the manufacture of hydrochloric acid a chloride, either a natural salt or a waste product from some industrial operation, is used.

This acid was known to the ancients, and was made by them by fusing salt with green vitriol. It was only known in solution, and the gas was

not known until the time of Priestley. In the early days of the alkali industry the hydrochloric acid, a waste product formed in the production of sulphate, was a great nuisance, and caused the manufacturer trouble, as it would destroy vegetation for some distance around the plant. To prevent this, they built high stacks, to the height of 500 ft., so as to dilute the acid vapors; but this only served to widen the circle of destruction, which extended over a mile and a half from the works. Then they conducted the gas into underground cisterns and channels, absorbing the gas in water and discharging it into the nearest water course. This killed the fish and gave an acid water which would corrode the metal parts of ships. Then came the economic absorption by water and the utilization of the acid formed in the production of chlorine, which was consumed in the bleach manufacturing industry. Thus, the production of bleach was a natural outcome of the alkali industry, utilizing the waste acid from the salt cake apparatus. In this country hydrochloric acid is the principal product of the action of sulphuric acid on salt, and the sulphate is of secondary consideration. In England the method of condensation is by the use of coke towers, the acid vapors rising through a tall narrow tower packed with coke, and meeting a stream of water which flows down from the top. In Europe a train of earthenware Woulff bottles (bombonns) is used. In this country a combination process is generally employed, the gas first passing through a train of the Woulff bottles, and then into a coke tower. The water which enters the top of the coke tower flows through the Woulff bottles, and the strong hydrochloric acid is collected from the first bottle. Often fifty or more bottles being in the train, the acid liquid running from one bottle to another through overflow connections half way up the bottle, the connections being made with glass tubes, which discharge into the bottom of the receiving bottle. As the gas should be as cool as possible before it enters the condensers, long cooling pipes are introduced between the furnaces and the condensers.

In the description of the production of sulphate by the action of sulphuric acid upon salt, mention was made of the fact that the reaction takes place in two stages; first in the cold from the pan and second in the furnace proper. The hydrochloric acid which comes from the furnace is not as pure as that formed in the pan, and as a rule the two acids are run through separate condensing systems, and the resulting solutions collected separately and sold as different grade acids. That coming from the roaster will contain more iron, sulphuric acid, arsenic, and other impurities than the acid collected from the pan. Hydrochloric acid is rarely distilled, the pure acid being made from pure materials.

Very many attempts have been made and patents taken out for the conversion of hydrous magnesium chloride into hydrochloric acid and magnesia, by the application of heat, the equation $MgCl_2+H_2O=MgO+2HCl$ being usually given to express the change. So far all these attempts have proven successful only in part. The temperature required,

the cost of labor in removing the residue from the furnace, and the fact that the reaction does not take place as written, but with the formation of an oxychloride which has little or no value, makes the process still imperfect.

Purification. Manufacturers have found it more profitable to make pure acid from pure new material than to purify crude acid. Sulphuric acid is removed by adding to the acid, as it comes from the absorbers, ground barium carbonate, allowing to settle and then decanting. Arsenic is removed by washing with coal oil in a tower between the furnace and the absorbers.

One method of purification consists in running the crude hydrochloric acid in a thin stream into hot vitriol. The gaseous acid driven out, is passed through lead pipes and absorbed in pure water running through lead towers packed with pure quartz, or well-washed coke. The sulphuric acid, being concentrated by heating, can be used over again.

Uses of Hydrochloric Acid. Hydrochloric acid is used in "pickling" iron for tinning, in the making of chlorides and of chlorine, in the production of glue, in the preparation of fatty acids from the lime soap, and for various other purposes.

X

COMMERCIAL CHEMICALS

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Sodium Carbonate. Before 1791 sodium carbonate was obtained from natural deposits and the ashes of marine plants. At the time of the French Revolution Leblanc brought forward his method for the commercial production of soda from salt. The process, which was introduced in 1791, held sway without competition until 1863, when the Solvay process (ammonia-soda) made its appearance. This would probably have entirely replaced the Leblanc process were it not for the valuable byproduct, hydrochloric acid, which is formed during the operation of the latter. At present the Leblanc process furnishes a little less than half of the sodium carbonate consumed.

Leblanc Process. By the action of sulphuric acid on common salt sodium sulphate is obtained. The sodium sulphate is then transformed into carbonate by the action of carbon and calcium carbonate; the reactions involved being represented by the following equation:

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl,$$
$$Na_2SO_4+2C=Na_2S+2CO_2,$$
$$Na_2S+CaCO_3=Na_2CO_3+CaS.$$

Preparation of Sodium Sulphate or Salt Cake. The reaction takes place in two stages, viz.:

$$NaCl+H_2SO_4=NaHSO_4+HCl,$$
$$NaCl+NaHSO_4=Na_2SO_4+HCl.$$

The furnace used for this purpose is described at another place. The first reaction takes place at a comparatively low temperature and at the back of the furnace; when it slackens the charge is raked forward, and is exposed to a higher heat when the second reaction takes place. The sulphuric acid should be at a strength between 57° and 60° Bé. Below 56° Bé. it would attack the cast-iron pan of the furnace, and above 60° Bé. it forms lumps of salt with an anhydrous coating of sodium sulphate. This coating prevents the penetration of the acid, thus making the action irregular and incomplete.

Conversion of Salt Cake into Carbonate. The salt cake should contain no sodium chloride and but little free sulphuric acid. It should be porous and friable, for which purpose it is exposed to the action of the air for two or three days. It is now mixed with limestone and powdered coal, the proportions indicated by Leblanc being:

Sodium sulphate	100 parts
Calcium carbonate	100 parts
Carbon	50 parts

In practice it is usual to use an excess of limestone and coal. At the end of the operation, when the temperature has reached about 1000° C., the calcium carbonate in excess is decomposed with the formation of lime and carbon dioxide. The latter, coming in contact with the carbon, is converted into carbon monoxide; the blue flame which makes its appearance indicates that the reaction is completed. The passage of the carbon monoxide through the mass renders it porous. The limestone should be very pure, as silica and aluminium would cause the formation of silicates and aluminates. The coal should contain little or no nitrogen, as this gives rise to cyanides, which react upon iron to form ferrocyanides and, in small quantities, cyanates.

Black Ash. In the manufacture of black ash the mixture of sulphate, carbon and limestone is introduced into the back of a black ash or balling furnace, which is a long reverberatory furnace. The mixture is heated at a rather low temperature at first; then after some time the charge is raked forward, nearer the grate, where the temperature is much higher, reaching 1000° C. The mass is stirred until it stiffens and the blue flame appears, indicating the end of the reaction. It is now worked together into a ball and raked into wagons, where it rapidly solidifies. On exposure to the air for two or three days the small quantity of lime present slakes, rendering the mass friable and easier to lixiviate. The hand-worked furnace is being replaced by the revolving furnace, as shown in Fig. 21.

Good black ash is of a very dark brown or gray color with porous fracture. It contains about 45 per cent of sodium carbonate, 30 per cent of calcium sulphide, 10 per cent of calcium oxide, 6 per cent of calcium carbonate and small amounts of sodium silicate, sodium aluminate, sodium sulphide, sodium chloride, ferric oxide and coal, while very slight amounts of cyanide, ferrocyanide and thiosulphate are usually present.

Lixiviation of Black Ash. When properly made, black ash is easily extracted by Shank's process. The material is placed in tanks having false bottoms, and is systematically treated with water. The fresh water comes in contact with the nearly exhausted ash and as it becomes more concentrated it meets the fresh ash. The lixiviation should be done at as low a temperature as possible and the ash kept covered with water to avoid contact with the air. In case these precautions are not observed, secondary reactions take place, thus reducing the yield of sodium carbonate.

Purification and Evaporation of Tank Liquors. The principal impurities of tank liquor are caustic soda, sodium sulphide, sodium thiosulphate, sodium ferrocyanide, sodium ferro-sulphide and traces of other compounds. The liquor is allowed to clarify by sedimentation and is then passed through carbonating towers, where it trickles over porous substances and comes in contact with a current of carbon dioxide and air. The caustic soda and sodium sulphide is here converted into carbonate, the ferro-sulphide is decomposed, and any iron, silica and aluminium present precipitated.

Paulie's Process. In this process MnO_2, as Weldon mud, is added to the liquor and superheated steam and air are passed through it. Sodium sulphide is oxidized to sulphate, and any iron, silica, and aluminium precipitated.

In either case the purified liquor is evaporated in cast-iron pans. As it becomes concentrated a crystalline powder separates, Na_2CO_3,H_2O, which by calcination at a red heat is converted to Na_2CO_3. The mother liquor (red liquor) is further purified or used for the production of caustic soda. This red liquor usually contains a large amount of caustic soda and sodium sulphide.

Instead of calcining the Na_2CO_3,H_2O, it may be converted into soda crystals (sal soda) by dissolving in hot water and allowing it to crystallize slowly. In this way large, nearly pure, crystals of $Na_2CO_3,10H_20$ are formed.

Treatment of Tank Waste. Fresh tank waste contains from 35 to nearly 60 per cent of calcium sulphide. To abate the nuisance from the ill-smelling H_2S gas, and to save the large amount of sulphur annually lost, manufacturers have endeavored to recover it. Thus far, however, the processes proposed have not fulfilled expectations and none are looked upon as of great practical value.

Mond's Process. As the most promising of these methods of recovery, however, may be mentioned Mond's process. In this the waste is treated in the lixiviating tanks with a strong air current, the calcium sulphide being verted mostly into calcium sulph-hydrate and calcium polysulphides. The liquor thus obtained is treated with hydrochloric acid at a temperature of between 40° and 60° C. The reaction may be expressed as follows:

$$CaS_2O_3+2CaS_n+6HCl=3CaCl_2+3H_2O+S_{2n+2}.$$

Schaffner and Helbig's Process. In this process the calcium sulphide is decomposed by magnesium chloride at boiling heat.

$$CaS+MgCl_2+H_2O=CaCl_2+MgO+H_2S.$$

The H_2S by incomplete oxidation produces sulphur or may be completely burned, the sulphur dioxide formed being used in the manufacture of sulphuric acid. The magnesium oxide suspended in the solution of

calcium chloride on being treated with a current of carbon dioxide will regenerate the magnesium chloride and cause a precipitation of calcium carbonate at the same time.

The Chance-Claus Process. In this process the tank waste is treated with a current of carbon dioxide. The principal reactions are as follows:

$$2CaS+H_2O+CO_2=CaCO_3+Ca(SH)_2,$$
$$Ca(SH)_2+CO_2+H_2O=CaCO_3+H_2S.$$

The H_2S mixed with the proper amount of air to give the reaction $H_2S+O=H_2O+S$ is submitted to incomplete combustion by passing it through a Chance-Claus sulphur kiln where it is led through a layer of broken firebrick covered with a layer of ferric oxide about one foot deep. After starting the reaction, the heat generated is sufficient to keep the ferric oxide at a dull red heat, at which temperature the process is continuous.

Processes have also been brought forward by Gossage, Schaffner, Haddock and Leith, and several others, but none of them pay well, and can only be looked upon as methods of doing away with the nuisance when the waste is allowed to accumulate.

Ammonia Soda or Solvay Process. This process was introduced by Solvay in 1863, and has been worked successfully since about 1873. It consists in reacting upon sodium chloride in a cold solution with hydrogen ammonium carbonate:

$$NaCl+NH_4HCO_3=NaHCO_3+NH_4Cl.$$

The sodium hydrogen carbonate (bicarbonate) is calcined, which decomposes it into sodium carbonate, carbon dioxide and water. By treating the ammonium chloride formed in the first reaction with lime, the ammonia is regenerated. The carbon dioxide is derived in part from the calcination of the sodium bicarbonate and partly from limestone, which furnishes also the lime for the regeneration of the ammonia from the ammonium chloride. The process is more economical than the Leblanc, the product is purer and there is no troublesome byproducts such as tank waste.

In conducting this process a pure concentrated brine solution is saturated with ammonia. The brine is contained in tanks with perforated false bottoms, through which the ammonia is forced in the form of a gas. When the brine is thoroughly saturated with the gas it is run into the carbonating tower. The tower consists of a cast-iron cylinder 40 to 60 ft. high and 5 to 6 ft. in diameter. At intervals of 3 to 3½ ft. there are fixed plates with a central opening. Over these plates are placed dome-shaped diaphragms, which are perforated with numerous small holes. The ammoniacal brine is forced under pressure into the carbonating tower through a pipe which enters near the middle of the tower. The carbon dioxide, at a pressure of 25 to 30 lbs., is forced into the lower end of the tower and allowed to bubble through the many perforated diaphragms; its expansion

as it enters the tower produces a cooling effect which prevents any great rise in temperature.

$$NaCl+NH_3+H_2O+CO_2=NH_4Cl+NaHCO_3.$$

The bicarbonate of soda being insoluble in the ammonium chloride solution is precipitated, drawn off, filtered, washed with cold water and calcined in cast-iron pans. The carbon dioxide liberated from the bicarbonate is pumped to the carbonating tower, and any ammonia given off is condensed and returned to the ammonia stills. The gases issuing from the carbonating tower are also condensed to recover any ammonia which they contain. The temperature of the solution in the carbonating tower should be carefully controlled, 30° to 35° C. being the temperature most favorable for the action.

The soda ash produced by the calcination of Solvay process bicarbonate of soda is white and usually very pure, containing only traces of salt and sodium bicarbonate.

Sodium Bicarbonate. Most of the sodium bicarbonate on the market is produced by the Solvay process. It is used in the manufacture of baking powders, soda water, and other products which require a mild alkali.

Caustic Soda. This product is prepared by causticizing sodium carbonate with lime. The purified tank liquor, which must be kept at a specific gravity of 1.1, is treated with lime at a boiling temperature. Water or dilute liquor must be added in order that a reverse action will not take place. In the Thomas process the reaction may be carried out in a concentrated liquor, under pressure and at a temperature between 140° and 145° C. The calcium carbonate is allowed to settle and the supernatant liquor is filtered through sand and carbon. The solution of caustic soda is evaporated in cast-iron kettles until all of the water is driven off and the alkali remains as a fused mass. The lower compounds of sulphur, such as thiosulphate, may be oxidized by the addition of a small quantity of sodium nitrate. For transportation the fused caustic is run into sheet-iron drums, which are closed as soon as cold to prevent absorption of water and carbon dioxide.

Caustic soda may be purified by solution in pure alcohol which dissolves the sodium hydroxide, but not the carbonate. A still purer sodium hydroxide may be obtained by the action of metallic sodium on distilled water.

There are a number of electrolytic processes for the manufacture of caustic soda which are discussed in Chapter XI.

Cryolite Process. The reactions involved in this process are as follows:

$$3NaF,AlF_3+3CaCO_3=Na_3AlO_3+3CaF_2+3CO_2.$$

The sodium aluminate resulting from this fusion is decomposed in an aqueous solution by carbon dioxide:

$$2Na_3AlO_3+3CO_2=3Na_2CO_3+Al_2O_3.$$

The sodium carbonate formed by this process is very pure.

Potassium Carbonate. The use of the salts of potassium carbonate is somewhat limited. This has been especially the case since the introduc- of the Leblanc process for the manufacture of sodium carbonate. Although the carbonate of potassium may be obtained from wood ashes, beet sugar residues and wool scourings, by far the largest amount comes from the natural deposits found near Strassfurt, Germany. The deposit cons sts principally of potassium chloride, which on purification may be converted into the carbonate by the same methods as apply for the sodium salt.

Caustic Potash. This is made in the same manner as caustic soda, but being very deliquescent is usually prepared as it is needed for use.

Aluminium Sulphate. The sulphate of aluminium $Al_2(SO_4)_3$, $18H_2O$ is prepared from clay, bauxite or from the aluminium oxide obtained in the manufacture of soda by the cryolite process. The calcined clay is finely pulverized and treated with sulphuric acid (sp.gr.1.47). The mixture is heated to start the reaction, which soon becomes violent. At the end of the reaction a hard cake remains (alum cake), which contains the silica, iron and other impurities. From bauxite, it is prepared by adding enough sodium carbonate to the finely powdered mineral to form a mixture containing 1.2 molecules of sodium carbonate for every molecule of aluminium oxide. The mass, after fusion, is rapidly lixiviated and the solution of sodium aluminate thus obtained is filtered, concentrated to 35° Bé and treated with a current of carbon dioxide which precipitates the Al_2O_3 in a granular form. This precipitated oxide on dissolving in sulphuric acid produces a sulphate which contains not over .02 per cent of Fe_2O_3.

The aluminium oxide obtained in the cryolite process when dissolved in sulphuric acid produces a very pure form of aluminium sulphate.

Alum. Alums have the general formula $M'''_2(SO_4)_3$, $M'_2SO_424H_2O$.

Potash Alum. Potassium aluminium sulphate, $Al_2(SO_4)_3$, K_2SO_4, $24H_2O$, is obtained from alumite or alumstone, which is mostly found near Rome. The mineral is calcined at a moderate heat (about 500° C.), exposed, when moist, to the atmosphere for 3 or 4 months, and then lixiviated. The alum obtained by the evaporation of the wash waters contains a small amount of basic aluminium sulphate and crystallizes in cubes called Roman or cubical alum.

Alum may be obtained from alum shists or slates by roasting and subsequent exposure to the air. The iron sulphide present is oxidized to sulphate and sulphuric acid. This latter reacts on the aluminium silicate, forming sulphate of aluminium. The ferric sulphate formed attacks the aluminium compounds, producing aluminium sulphate and basic ferric sulphate. The mass is washed and the solution evaporated to 40° Bé. Most of the iron compounds crystallize out, and are separated. The proper amount of potassium sulphate in concentrated solution is now added when the alum begins to separate. The crystalline product obtained still contains some iron and must be purified by recrystallization.

Alum may be readily obtained by adding the proper amount of potas-

sium sulphate to a concentrated solution of aluminium sulphate and allowing it to crystallize out.

Sodium and Ammonium Alums. These alums may be obtained by using sodium or ammonium sulphate in place of potassium sulphate. These products all have nearly the same chemical and physical properties, being colorless, soluble salts which crystallize in octahedra.

Aluminium Acetate. This compound usually is found on the market in a liquid condition known as "red liquor." It may be prepared either by acting upon aluminium hydroxide with acetic acid, or by double decomposition of aluminium sulphate with calcium acetate. It is principally used as a mordant in dyeing and printing and in the water-proofing of tissues.

Ammonia. When animal matter undergoes decomposition, more or less ammonia is produced. It is also formed when nitrogenous organic substances are subjected to destructive distillation. By means of the latter process, during the distillation of coal for the production of illuminating gas and coke, most of the ammonia of commerce is produced. To a limited extent ammonia is also obtained from the distillation of bones and other animal matter, from putrid urine, sugar residues, and from waste furnace gas. It is likewise possible to obtain ammonia by passing air over a mixture of barium oxide and carbon heated to a white heat, but the process has never met with commercial success.

The nitrogen in the ammoniacal liquor of the gas works is present in the form of free ammonia, ammonia combined as carbonate, sulphide, sulphyhydrate, sulphite, sulphocyanide and ferro-cyanide. As the liquor comes from the hydraulic main, the scrubbers and condensers, it is mixed with a large amount of tarry matter, which, on standing, settles out, leaving a fairly clear liquid which may be treated for its ammonia content. There are various methods employed for recovering the ammonia, but the one in common use is that in which the Feldman's apparatus is employed: The settled gas liquor passes by means of a series of narrow tubes through a cylindrical chamber, where it becomes somewhat heated from the waste gases passing through this chamber, which is known as the "economizer." The heated liquor is then forced to the top of a tall tower, where it meets a current of steam which causes volatile ammonia compounds to be liberated. The non-volatile compounds flow down the tower and coming into contact with boiling lime water free ammonia is produced. The free and volatile ammonia compounds are next caused to pass through a large pipe into the absorption vessel containing sulphuric acid. Here the sulphides and other volatile salts of ammonia are decomposed with the formation of ammonium sulphate and the liberation of hydrogen sulphide and carbon dioxide. These hot gases thus formed are collected in the dome over the absorption vessel and from there pass into the shell of the economizer, producing the heat referred to above. The waste sludge from the lime treatment is drawn off from time to time

and the liquor in the absorption vessel concentrated as it becomes saturated, being sold as crude ammonium sulphate.

On recrystallizing the crude ammonium sulphate and redistilling with lime, a pure gas is obtained which, being absorbed in water, forms the "aqua ammonia" of commerce, or the ammonium hydroxide of the laboratory. By subjecting ammonia gas to high pressure it is possible to convert it into a liquid. Liquid ammonia has extensive application at present, being used for producing cold in ice machines.

Ammonium Chloride. This compound is manufactured either by absorbing the gas in dilute hydrochloric acid, or by neutralizing the gas liquor directly with the acid. In either case the resulting solution is evaporated to obtain the crystals, which is then purified by recrystallization or sublimation. Ammonium chloride is usually purified, however, by sublimation, in which case it is heated in iron or earthenware pots provided with a dome-shaped cover. The purified product collects in the dome as a thick crystalline cake which is removed and placed on the market as *sal-ammoniac.* Formerly this salt was made by burning dried camel's dung, but at present it is all prepared from gas liquor.

Ammonium Carbonate. The commercial product is prepared by heating a mixture of the sulphate of ammonia and powdered calcium carbonate in iron retorts and collecting the sublimate formed in lead-lined chambers. The product thus obtained is a mixture of ammonium bicarbonate and ammonium carbamate.

Ammonium Nitrate. This salt is prepared in a manner similar to that employed in making the chloride, except that it cannot be purified by sublimation. Its chief uses are in the manufacture of explosives and for making nitrous oxide, so-called laughing gas.

Ammonium Sulphate. The crude salt is dark brown in color and is prepared as described under ammonia. Its chief use is as a base for making other ammonia salts, and in the impure form for the manufacture of fertilizer. When purified it gives a white crystalline product used for fire-proofing fabrics as well as for other purposes.

Antimony Fluoride. The compound SbF_3 is prepared by dissolving antimony oxide in hydrofluoric acid. This salt readily forms double compounds with alkaline sulphates and chlorides. $(NH_4)_2SO_4, SbF_3$, is an example of these double salts and is one of the important mordants. The double fluoride of ammonium and antimony $8SbF_3, 2NH_4F$ is a useful salt. These compounds are used as mordants, and have, to a great extent, replaced tartar emetic.

Arsenious Oxide. White arsenic, As_2O_3, is obtained by roasting arsenical minerals, such as mispickel FeAsS, cobaltite CoAsS, smaltite $CoAs_2$ and other minerals containing arsenic. The roasting is carried on in reverberatory furnaces with free access of air and the sublimed arsenic trioxide condensed in suitable chambers. It is purified by resublimation and collected as a white powder. By resublimation under pressure it is

obtained in a vitreous variety known as arsenic glass. It is usually ground to a fine powder, which is slightly soluble in water. It is principally used as an antiseptic for preserving hides; it also finds application in glass manufacture, and its glycerine solution is used in calico printing.

Arsenic Acid. By oxidizing arsenic trioxide with nitric acid the compound H_3AsO_4 is obtained as a thick syrupy liquid.

Sodium Arsenate. By fusing together a mixture of arsenic trioxide and sodium nitrate the compound Na_2HAsO_4 is obtained.

Chrome Alum. The compound $Cr_2(SO_4)_3$, K_2SO_4, $24H_2O$ is obtained as a byproduct in many operations where a mixture of potassium dichromate and sulphuric acid is used as an oxidizing agent. It is used as a mordant, and in certain chrome tannages.

Chromium Acetate. This compound comes to the market as a neutral and basic salt. It may be prepared by the same process as described for aluminium acetate, or it may be prepared from sodium dichromate and acetic acid in the presence of a reducing agent.

Potassium Dichromate. The material which is used to furnish the chromium is chrome iron ore or chromite. The ore is finely pulverized and mixed with lime and sodium carbonate. A small amount of calcium carbonate is usually added as the carbon dioxide liberated renders the mass porous. This mixture is heated in a reverberatory furnace in the presence of a strong current of air. At the end of the reaction the mass consists of a mixture of calcium chromate, sodium carbonate and ferric oxide, which, being lixiviated, yields sodium chromate and insoluble calcium carbonate and ferric oxide. The solution is now neutralized with sulphuric acid, which precipitates the alumina and silica. It is then filtered and evaporated. When the concentration reaches a specific gravity of 56° Bé, the requisite amount of sulphuric acid is added and the chromate is converted to dichromate:

$$2Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + Na_2Cr_2O_7 + H_2O.$$

Most of the sodium sulphate is precipitated by this treatment, and may be separated by filtration. The solution is then concentrated to 60° Bé, when more sodium sulphate separates, and on allowing it to stand the sodium dichromate crystallizes. From this sodium dichromate the potassium salt is obtained by double decomposition. The workmen must avoid breathing the dust or vapor containing chromates, as they attack the cartilages of the nose and throat.

The residue of chromium oxide from alizarine manufacture is utilized in preparing dichromate. It is mixed with lime and moulded into bricks, which are subsequently calcined in a current of air. In this treatment calcium chromate is formed, which may be converted into the potassium salt by treatment with potassium carbonate.

Potassium dichromate forms large orange-colored crystals, melting at 400° C. and decomposing at a red heat into Cr_2O_3 and K_2CrO_4. It is used

in making chrome yellow, Guignet's green, as a discharge, in bleaching oils and fats, in chrome tannage and as an oxidizing agent.

Sodium Dichromate. The manufacture of this compound has been given above. On account of its cheapness it has to a large extent replaced potassium dichromate. It is very deliquescent, but if dried at 200° C. it loses water of crystallization and becomes anhydrous, in which condition it is no longer deliquescent. It is more soluble than the potassium salt and is used for the same purposes.

Copper Sulphate. This compound is also known as blue vitriol and as bluestone. It is obtained as a byproduct in the parting of gold and silver by the action of boiling concentrated sulphuric acid, the silver being dissolved as sulphate. The metallic silver is recovered by precipitating it with metallic copper. Copper sulphate may be produced by treating scrap copper with a spray of dilute sulphuric acid in the presence of air. Scrap copper mixed with sulphur and heated to a dull red heat yields copper sulphide. This compound heated in the air is converted into sulphate and oxide:

$$Cu_2S + O_5 = CuSO_4 + CuO.$$

The copper oxide treated with warm sulphuric acid dissolves, forming more copper sulphate. By the oxidation of some of the natural sulphides of copper a mixture of sulphate of copper and sulphate of iron is obtained. These sulphates, being isomorphous, cannot be separated by crystallization, but by oxidation of the ferrous to the ferric sulphate a mixture is produced which may be separated by crystallization.

Copper sulphate forms blue crystals, which are soluble in water. Heated to 240° C. it loses its water of crystallization and becomes a white anhydrous powder with a very strong affinity for water. Blue vitriol is used as a mordant, in the preparation of insecticides and in germicides, in electrolytic operations and for many other purposes.

Ferrous Sulphate. This compound, also known as copperas and as green vitriol, is obtained as a byproduct in the manufacture of cement copper. In this process the copper is precipitated from a solution of its sulphate by means of iron. The ferrous sulphide, obtained from the distillation of pyrites in the process of extracting sulphur therefrom, may be allowed to weather in the presence of moisture, by which means both ferrous and ferric sulphates are formed. To the mixed sulphates, scrap iron and sulphuric acid are added, which reduces iron from the ferric to the ferrous condition. A large amount of ferrous sulphate is obtained from the pickle used in cleaning iron castings.

The solution of ferrous sulphate obtained by any of the above methods is concentrated by application of heat to the surface or the liquid which thus prevents oxidation. The concentrated solution is allowed to crystallize on wooden rods. The crystals of ferrous sulphate effloresce in the air and become more or less oxidized, basic ferric sulphate being formed. It

is soluble in about 1½ parts of water. Ferrous sulphate finds its most important use as a mordant, as a disinfectant, in the manufacture of ink, Prussian blue, and red oxide.

Ferric Sulphate. This may be prepared by the weathering of pyrites in the presence of sulphuric acid. It may also be made by adding sulphuric acid and nitric acid to a solution of ferrous sulphate. Its principal use is as a sewage precipitant.

Ferric Nitrate. By treating scrap iron with an excess of nitric acid (sp.gr. 1.3) and evaporating the solution, colorless crystals are obtained. By adding ferric hydroxide to this solution a basic nitrate is obtained. This basic nitrate is used in silk dyeing and weighting and for coloring buff on cotton. The usual form of "nitrate of iron" consists of basic sulphate of iron containing oxides of nitrogen. It is used in silk dyeing.

Ferrous Acetate. This is prepared by adding lead or calcium acetate to a solution of ferrous sulphate. An impure product, known as "black iron" or "iron liquor," is made by adding scrap iron to crude pyroligneous acid. Its principal use is as a mordant in leather dyeing and in calico printing.

Magnesium Sulphate. Epsom salts is found in many mineral springs, but the most important source is Kieserite ($MgSO_4$, H_2O), which is quite insoluble in water, but on standing in contact with water for some time it undergoes solution, becoming $MgSO_4$, $7H_2O$. It is also prepared from Kainite (K_2SO_4, $MgSO_4$, $MgCl_2$, $6H_2O$), and is easily obtained by action of sulphuric acid on the natural carbonate, magnesite. It is a colorless crystalline salt, readily soluble in water and efflorescent in dry air. It loses all of its water of crystallization at about 230° C.

Silver Nitrate. By dissolving pure silver in dilute nitric acid silver nitrate is obtained. If a copper-silver alloy is used, the copper may be eliminated by evaporating to dryness and heating the dry mass to a temperature of 250° C. The copper nitrate is decomposed, yielding copper oxide, and as the silver nitrate is not affected, it may be dissolved in water and the solution evaporated to crystallization. It is a colorless salt, soluble in water, melts at 225° C. and decomposes at dull red heat. It is used as a cautery, in photography, in the preparation of indelible ink and for silvering the back of mirrors.

Lead Nitrate. By dissolving litharge in dilute nitric acid and evaporating to a small volume colorless crystals of lead nitrate are produced. By treating with an excess of litharge the basic nitrate is formed.

Stannous Chloride. The hydrated salt, $SnCl_22H_2O$, is prepared by the solution of the metal in concentrated hydrochloric acid, aided by moderate heat. The addition of a little nitric acid facilitates the reaction. The solution is concentrated by evaporation, cooled and allowed to crystallize. When dissolved in water it undergoes partial decomposition with the formation of an insoluble oxychloride. It is a valuable mordant and is used as a weighting material for silk, and in calico printing.

Stannic Chloride. The hydrated compound is obtained from the

mother liquor of stannous chloride by the progressive addition of nitric acid; the resulting liquid is concentrated and the stannic chloride allowed to crystallize. The penta hydrate, $SnCl_4$, $5H_2O$, may be prepared by passing chlorine through the mother liquor from stannous chloride. Its principal use is that of a mordant.

Sodium Stannate. The salt, Na_2SnO_3, $3H_2O$, may be obtained by fusing sodium hydroxide and metastannic acid together, or by boiling tin scrap with sodium plumbite. It is known as preparing salt, and is used as a mordant. Solutions of tin in sulphuric acid and oxalic acid are known in the trade as tin spirits, and used for mordanting.

Zinc Sulphate. White vitriol, $ZnSO_4$, $7H_2O$, is prepared by dissolving scrap zinc in dilute sulphuric acid. Upon evaporation a white crystalline product separates. It is used to some extent in calico printing and in dyeing, as a drier for linseed oil, as a disinfectant, and as an astringent.

Potassium Ferrocyanide. The oldest method of manufacture consists in heating a mixture of scrap iron with organic compounds containing nitrogen, such as horns, hoofs, hides, dried blood and potassium carbonate. The modern method is to fuse potassium carbonate in iron crucibles and add in small portions the nitrogenous material. The action is very violent, and must be conducted with care. After the reaction is completed the fused mass is lixiviated to separate the ferrocyanide from the carbonaceous matter. The solution is evaporated to a sp. gr. of 1.27, when the ferrocyanide crystallizes out. As the first product is very crude, it must be subjected to recrystallization.

Cyanamide. On heating lime and carbon in an electric furnace in the presence of nitrogen calcium cyanamide is formed:

$$CaO+2C+2N=CaCN_2+CO.$$

In the process of lixiviation the cyanamide is converted into dicyanamide:

$$2CaCN_2+4H_2O=2Ca(OH)_2+(CNNH_2)_2,$$

which yields oxamide when fused with potassium or sodium carbonate..

$$(CNNH_2)_2+Na_2CO_3+2C=2NaCN+NH_3+H+3CO+N.$$

The ammonia formed is recovered. Ortlieb and Muller utilize the residues of sugar extraction. The calcination of the vinasses in beet sugar manufacture yield amines which by high heat are converted into ammonium cyanide, hydrocyanic acid, hydrogen and carbon. The products of the calcination are passed through a cylinder heated to redness, then through a solution of sulphuric acid to absorb the ammonia, and finally through a solution of caustic potash to absorb the hydrocyanic acid. Cyanides may also be prepared from the hydrated ferric oxide used in the purification of illuminating gas.

Potassium Ferricyanide. This is prepared by acting upon the ferrocyanide with a current of chlorine:

$$K_4Fe(CN)_6+Cl=KCl+K_3Fe(CN)_6.$$

Potassium Cyanide. By fusing potassium ferrocyanide with potassium carbonate a change takes place resulting in the formation of potassium cyanide and potassium cyanate; the latter being mostly eliminated by the addition of carbon during the reaction.

Boric Acid. This compound, also known as boracic acid, is found in the steam which issues from fissures in the earth in the vicinity of volcanoes. The steam is condensed in reservoirs of water built around the points from which it issues. When the water has become fairly well saturated it is allowed to settle and then transferred to lead-lined tanks, where it is concentrated to a specific gravity of 1.08. The boric acid which crystallizes is usually purified by recrystallization. Some boric acid is obtained by decomposition of borax with hydrochloric acid. It is a colorless crystalline solid, slightly soluble in cold water, but readily solublein hot water. It is used as a flux, in the manufacture of borax, in fusible glazes, in special optical glass, and as an antiseptic and preservative.

Borax. Sodium tetraborate may be prepared by neutralizing boric acid with sodium carbonate. The chief source of borax, however, is from the natural deposits of Thibet, and from the crude borax of California. Crude borax is purified by slow recrystallization. The most common form is the prismatic $Na_2B_4O_7$, $10H_2O$, which effloresces in the air and melts in its water of crystallization, becoming anhydrous at a red heat. Borax is used as a flux, in glass and enamel making, in them anufacture of soap and as a preservative.

Phosphorus. Tribasic calcium phosphate $Ca_3(PO_4)_2$ in the form of bone, bone ash and mineral phosphate is the source from which phosphorus is manufactured. The finely ground material is treated with sulphuric acid (sp.gr. 1.52) in lead-lined tanks. This converts the tricalcium phosphate into monocalcium phosphate. The clear solution is drawn off and the precipitate thoroughly washed with hot water. The solution and washings are evaporated in leaden pans to 45° Bé, about 25 per cent of coke or charcoal added and the pasty mass dried in iron pans. The dry mixture is then subjected to distillation in fireclay retorts, usually placed in two tiers. At the start of the operation the monocalcium phosphate is changed to the metaphosphate, which in the presence of carbon forms tricalcium phosphate, phosphorus and carbon monoxide. The neck of the retort is passed into a condenser containing water, under which the phosphorus collects. By this method about two-thirds of the phosphorus in the phosphate is set free.

Electrical processes are taking the place of the older methods for the manufacture of phosphorus. A charge of the mineral phosphate, coke

and sand is heated in an electric furnace and results in a yield of about 86 per cent.

The crude phosphorus is purified by filtration through porous tile, chamois skin, or canvas; this operation being carried on under warm water, which keeps the phosphorus liquid. It may also be purified by melting under a warm solution of potassium dichromate and sulphuric acid. In Germany it is usually purified by redistillation in iron retorts.

Ordinary phosphorus is a yellow, wax-like solid, which melts at 44° C., has a specific gravity of 1.82, and distills at 269° C. It appears on the market in the form of sticks; which, being highly inflammable, have to be kept under water.

Red Phosphorus. The amorphous form is prepared by heating ordinary phosphorus in closed iron pots to a temperature of 250° C. for several days, as there always remains some unchanged phosphorus which must be removed by treating the mass with boiling caustic soda or carbon disulphide. Thus obtained it is a reddish-brown substance, which only inflames in the air when heated to about 260° C. It is insoluble in water, carbon disulphide and, unlike ordinary phosphorus, is not poisonous.

Ordinary phosphorus is used in making matches and phosphor bronze; while the red variety is used in the manufacture of safety matches.

Phosphoric Acid. This acid is prepared from bone ash or mineral phosphate by the action of sulphuric acid. The filtered solution is concentrated to a syrupy consistency, which contains about 85 per cent of H_3PO_4. If further heated it loses one molecule of water and becomes metaphosphoric acid, which is called glacial phosphoric acid.

Water Glass. Soluble glass or water glass consists of soluble silicates of sodium or potassium or a mixture of the two. It usually comes on the market as a thick syrupy liquid. In its manufacture a mixture of sand, charcoal and soda is heated together in a reverberatory furnace for eight to ten hours. The glass-like mass is broken up and boiled with water. The solution obtained is filtered and concentrated to the proper consistency.

Water glass is used to render tissues non-inflammable, to protect wood and porous stone, as an addition to cheap soaps, to fix pigments on calico, in the manufacture of artificial stone, as a fixative in mural paintings, also as a cement for glass and pottery.

Oxygen. Only a few of the methods devised for the industrial preparation of oxygen have proved of practical and of economic value.

Boussingault-Brin Bros. Process. In the original process barium oxide is heated to a dull redness in a current of air, which has been freed from carbon dioxide. At this temperature it absorbs oxygen and becomes barium peroxide. When the reaction is completed the heat is raised to bright redness when it is dissociated into barium oxide and oxygen. The barium oxide can be used again and the process would be continuous if the barium oxide did not become glassy and hydrated. For this reason the

process is not practical, as the reaction cannot be repeated successfully more than ten or twelve times.

Gondolo proposed the intimate mixing of lime or magnesia with the barium oxide. This prevents, to a certain extent, the production of hydrate, so that the operation may be repeated 125 times.

The modification introduced by the Brin Brothers consists in heating the barium oxide to a dull redness in retorts into which pure air is forced under a pressure of about 15 lbs. to the square inch. When the barium oxide has been converted to the peroxide the pressure pump is reversed and a vacuum of about 27 ins. produced, the temperature remaining the same. Under these conditions one atom of oxygen is evolved from the barium peroxide. The operation is a continuous one, except that the barium oxide must be revivified every six months.

Thessie du Motay-Marechal Process. In this process a mixture of manganese dioxide and caustic soda is heated in a current of dry air to dull redness, sodium manganate being formed. The properly granulated mass is now heated to 450° C. in a current of steam, when the following reaction takes place:

$$Na_2MnO_4 + H_2O = 2NaOH + MnO_2 + O.$$

To secure regularity in the reaction a small amount of cuprous oxide may be added to the mixture. As manganese dioxide and sodium hydroxide are regenerated in the second reaction the process is a continuous one.

Oxygen from Liquid Air. The machines for the production of liquid air have been perfected so that its production has become very economical. If liquid air is allowed to evaporate the nitrogen passes off more readily than the oxygen. By use of doubled-walled vacuum vessels the evaporation takes place so slowly that most of the nitrogen escapes, leaving fairly pure oxygen. By this method oxygen gas containing about 10 per cent of nitrogen may be obtained.

Oxygen is used in the oxy-hydrogen blow pipe, in the manufacture of blown oils, in the aging of liquors, in refining of glass, in medicine and in the oxy-acetylene welding process.

Ozone. This gas is produced on a fairly large scale for bleaching purposes by passing air through an electrical machine which is provided with a series of vacuum tubes, such as used for X-ray production.

Alkaline Peroxides. By heating 100 parts of alkali with 70 to 90 parts of lime or magnesia to a temperature of bright redness an alkaline oxide is formed. The alkaline oxide, heated in a current of dry air at a temperature of about 500° C., is converted into the peroxide. The pulverized mass is slowly added to water and after the elimination of the lime or magnesia yields a solution which can be used for bleaching. By the addition of soluble salts of calcium, barium or strontium to this solution the peroxides

of the alkaline earths are precipitated. The alkaline peroxides may also be prepared by exposing the fused metal at a temperature of 300° C. to a current of purified, dry air.

Hydrogen Peroxide. This is prepared by the action of dilute acids on barium peroxide. A mixture of the peroxide and water of the consistency of a cream is prepared; this is added slowly to cold dilute phosphoric acid, the temperature of which should not rise over 15° C. After the proper amount has been added the precipitate of barium phosphate is allowed to settle and the clear liquid decanted. It is best to have the acid in slight excess, as the solution is less liable to decompose.

Peroxides are strong oxidizing agents. Hydrogen peroxide, however, acts as a reducing agent in the presence of certain oxidizing substances, in which the oxygen is closely linked. It is used in the bleaching of silk, wool, hair, feathers and ivory. It is a powerful antiseptic and is used in surgery and to prevent processes of fermentation.

Fixation of Nitrogen. By passing an electric spark through air it is possible to combine the nitrogen and oxygen present. This is being carried on commercially by the Badische Aniline- und Soda-fabrik Company, and consists in passing the air, with a rotary motion, over a series of high intensity alternating-arcs contained in a small iron tube. The gases produced are absorbed by lime water, thus giving a mixture of calcium nitrite and nitrate. The product after evaporation is brought to the market as Air Salt-peter.

Carbon Disulphide. This compound is prepared by passing the vapor of sulphur over highly heated charcoal. Vertical iron or clay retorts are usually employed, and the sulphur introduced through a tube on the side. The uncombined sulphur is collected in a special receiver, while the carbon disulphide passes on and is condensed. The product thus obtained is very impure, and must be purified by treating with lead acetate, then with lime water and finally by redistilling. When pure, carbon disulphide is a nearly colorless mobile liquid, with only a slight odor. The commercial article, however, has a very disagreeable odor, due to the presence of sulphur compounds. It is heavier than water, boils at 46.5° C., and its vapor inflames at 149.5° C. It is a good solvent for sulphur, phosphorus, resins, waxes and fats. It is also used, to some extent, as a germicide and insecticide.

Carbon Tetrachloride. This compound is made by passing the vapor of carbon disulphide and dry chlorine through a heated earthenware tube; or it may be prepared by passing chlorine over liquid carbon disulphide in which a little iodine has been dissolved. Sulphur monochloride is formed at the same time and is removed from the carbon tetrachloride with milk of lime and potash, and then distilled. Carbon tetrachloride is a non-inflammable heavy liquid, having a specific gravity of 1.637 and a boiling-point of 76.5° C. It is a good solvent for gums and resins and is also largely used in cleaning solutions.

Sulphur Monochloride. To prepare this compound a current of chlorine is passed over melted sulphur, which is heated to about 130° C. Chloride of sulphur mixed with sulphur, distills over and is purified by redistillation. It is a somewhat oily liquid of a yellowish-brown color, having a suffocating odor and boiling at 144° C. When brought in contact with water it decomposes with the formation of hydrochloric acid, sulphur, sulphurous acid and a small amount of sulphuric acid. Its chief use is in the vulcanization of rubber and in the manufacture of rubber substitutes.

Acetone. Acetone occurs in the liquid obtained from the destructive distillation of wood. It is usually made, however, by the dry distillation of gray lime (crude acetate of calcium) at a temperature of 290–350° C. In the Squibb process the vapor of acetic acid is passed over porous baryta heated to a temperature of 350° to 400° C. The product of the reaction is passed into a fractional condensing apparatus which removes water and undecomposed acetic acid. Acetone is a colorless liquid having an ethereal odor and boiling at 56° C. It is soluble in water, alcohol and ether. It is used as a solvent for gums and resins, and in the manufacture of chloroform, iodoform and sulphonol.

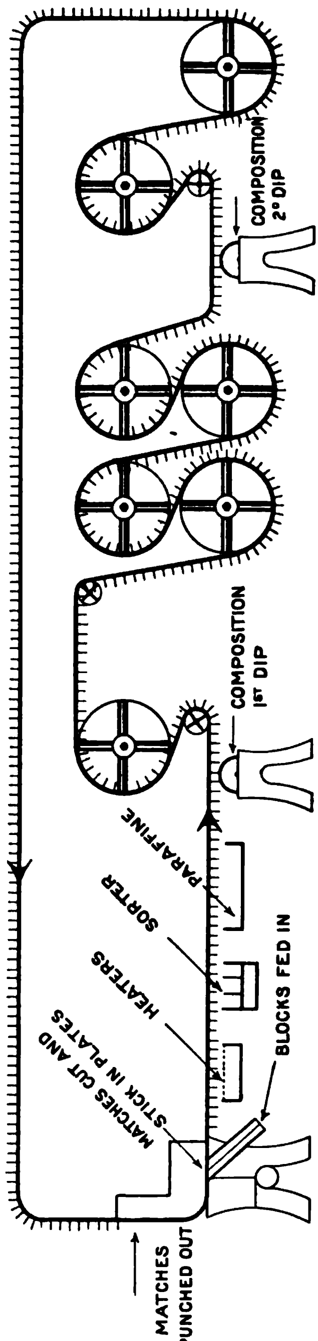

Fig. 157.

Matches. The first chemical matches were introduced in 1807 and known as "chemical tinder." They were made by saturating a portion of the splint in melted sulphur, provided with a head having a mixture of potassium chlorate and sugar. To light the match it was brought in contact with sulphuric acid, which caused a rapid decomposition of the chlorate causing the sulphur and sugar to burn. From this primitive, yet scientific discovery, the modern friction and safety matches have been evolved.

Double Dip Friction Match.[1] Perfectly dry white pine blocks are cut into $2\frac{3}{8}$-inch lengths. These blocks are then fed into the cutting machine[2] (Fig. 157) so that the grain stands in a vertical position to the knife, which is attached to a plunger and cuts forty match splints at a single stroke. The splints are automatically forced into the openings of perforated iron plates which are conveyed, by an endless chain, over a series of heaters so as to completely dry them. Adjoining the heater is a spring arrangement which forces out any thin or poor splints. The plates, now carrying only perfect match sticks, pass over the trough containing paraffin in such a manner that $\frac{1}{4}$ of the stick becomes impregnated. They next pass over the composition rollers, where a small amount of the composition is deposited on the end of each splint. The composition of the first dip consists of potassium chlorate, glue, flint and filler (such as clay for body). In order that the first dip may have time to dry the plates are made to travel up and down through a series of wheels and are then given a second dip on a machine similar to the first. The composition of the second dip consists largely of phosphorus, chlorate of potash, glue and filler. The finished match is now carried back to where it was cut, punched out into troughs and carried to the packers. The plate is refilled and the journey repeated. The advantage of the double dip match over the other forms is that the danger of flying off of the head is eliminated. The tip or second dip ignites on friction, the heat produced being sufficient to ignite the first dip, both of which burn quietly.

The machine used for double dip matches is 96 feet long, contains 1600 plates, takes one hour for the complete operation and makes 8,000,000 matches in 10 hours.

Single Dip Matches. The manufacture of matches by this process is the same as that above except that it is simpler, as only one dip is made. The composition of these matches consists of glue, potassium chlorate, phosphorus, flint and filler.,

Safety Matches. These are made in a manner similar to friction matches, except that the phosphorus is not present on the head of the match. In order to ignite to match it must be rubbed over a surface coated with phosphorus, which thus acts in a manner similar to the second dip on a friction match.

[1] D. A. Young, Ohio Match Company, Wadsworth, Ohio.
[2] J. R. M. Klotz, Barrett Mfg. Co., Philadelphia, Pa.

XI

CHLORINE AND ALLIED PRODUCTS

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Raw Materials. The primary raw materials of the chlorine industries are the alkali chlorides, common salt (chloride of sodium) and potassium chloride. Common salt, of high purity, is everywhere available at moderate cost, the most objectionable impurity being calcium sulphate. The cost of salt is about $4 per ton, f.o.b. works, but at the salt mines or brine wells it is much less. Potassium chloride occurs in commercial quantities only at the Stassfurth deposits in Germany. It is not usually as pure as common salt and contains considerable amounts of sodium and magnesium salts. Much potassium chloride is treated electrolytically in Germany for the production of caustic potash, the chlorine being delivered from the cells practically free of charge to the manufacturer, since the value of the caustic potash is sufficient to cover all the manufacturing costs and still leave a profit. This cheap chlorine is largely responsible for the rapid rise in the manufacture of bleaching powder and chlorine products in Germany.

A secondary raw material is hydrochloric acid, produced by the action of sulphuric acid upon common salt. It was formerly almost a waste product of the Leblanc process for manufacturing sodium carbonate, and is still available in England in enormous quantities at a very low price.

Sodium chloride is a very strong compound. Its heat of formation in the solid state is 97.7 cals. (kilogram calories) per gram equivalent (58.5 grams.):

$$NaCl + 97.7 \text{ Cals.} = Na. + Cl.$$

In liberating the chlorine this energy must be supplied, in the form of heat, by electricity or by the chemical energy generated by the formation of other compounds of sodium. In hydrochloric acid (heat of formation as gas+22 cals. in aqueous solutions+38.0 cals.) the chlorine is not so powerfully bound and less energy or power is necessary for its liberation.

The manufacture of caustic soda and chlorine directly from common salt has been accomplished only electrolytically. Theoretically the simplest process is the electrolysis of fused salt and conversion of the sodium produced to sodium hydroxide by reaction with water.

One gram equivalent of solid sodium chloride requires for decomposition into sodium and chlorine 97.7 cals. This is equivalent in electrical energy 407,084 joules (joules = amperes × seconds × volts) 1 joule = .00024 cals., therefore 97.7 cals. = 97.7 ÷ .00024 or 407,084 joules). We know from Faraday's law that for the electrolysis of one gram equivalent of any substance there is necessary 96,540 coulombs (coulomb = ampere × seconds). The electrical pressure must therefore be at least $\frac{407084}{96540} = 4.21$ volts in any system in which fused salt is the electrolyte and sodium and chlorine the primary products. This is the theoretical minimum. If electrical energy is consumed in overcoming the resistance of the bath, dissipated in the form of heat, or used up in the formation of byproducts, more energy will be required, as is indeed always the case in actual practice. The theoretical minimum, however, serves as a measure. If, for instance, in the electrolysis of fused salt 7.00 volts are required, the volt or pressure efficiency is 60 per cent. While a high energy efficiency is desirable it is by no means all important. Power is only one item of expense which is often overbalanced by the cost of labor, maintenance and materials.

Sodium chloride melts at 772° C. (dull red heat) and at this temperature is a good conductor of electricity. On passing an electrolytic current of sufficient voltage through fused salt gaseous chlorine is liberated at the anode and liquid metallic sodium at the cathode. The sodium, being lighter than salt, floats up through the bath, and unless immediately removed recombines with the chlorine or oxidizes in the air. Fused salt acts strongly upon most materials and the construction of a suitable container is a serious problem. The hot chlorine also acts upon metals and many anode materials. These various difficulties have been overcome in the Acker process, as follows:

Acker Process. In the Acker process, Fig. 158, solid salt is fused by passing through it a current of very high density. Chlorine is liberated at the anodes of Acheson graphite and is drawn off by a slight suction into brick conduits. Sodium is liberated at the cathode, a shallow body of molten lead, with which it immediately alloys. This alloy is fluid as long as the percentage of sodium is very low. The body of molten lead is kept in continuous motion in one direction and passes through a short connecting channel under the hearth to a second compartment called the well. It is here elevated by means of a sort of steam injector, which consists of a vertical cast-iron pipe dipping into the well and pointed upward. The well has a curved cast-iron cover. On admitting steam, the lead sodium alloy is projected upward against the face of the cover and decomposed into metallic lead, caustic soda and hydrogen. The products are deflected downward into a third small compartment, the caustic chamber. Here the lead sinks by gravity and flows back into the cell to take up more sodium and go the round anew. The caustic soda, being lighter, collects in an anhydrous condition at the top of the caustic chamber and overflows from a spout into a col-

lecting vessel. Any excess of steam with the hydrogen, which burns quietly, escapes at the same point. The action is entirely continuous. The rate of flow of the cathode lead is controlled by the rate of steam supply, which is usually a little greater than that theoretically necessary to convert the metallic sodium into hydrate. The bath of electrolyte is kept up to volume by periodically shoveling in solid salt. The cell or furnace is made of cast iron, that portion which contains the salt being lined with two rows of magnesia or ordinary firebricks laid in without bond. The molten salt penetrates between the cracks and freezes in the outer layer, making the lining impervious. Each cell is about 3×6 ft., and carries four anodes having an effective surface of about 3 sq. ft. in all. The under surface of the anodes are grooved to prevent the chlorine accumulating upon them, which would raise the resistance. The current is very high, 8300-8500 amperes, a current density of 2800 amperes per square foot. The voltage is about 6.5 volts under normal operating conditions. The output of each

Fig. 158.

cell is about 550 lbs. anhydrous sodium hydroxide and 495 lbs. chlorine per 24 hours. The caustic is very pure. It contains 1 per cent total impurities (a little salt which gets in mechanically and a little carbonic acid taken up from the air). It is collected in large pots holding from 10 to 13 tons, where it is kept molten to allow impurities to settle out and is treated with a little sodium hyposulphite to destroy traces of sodium manganate, etc., which gives it a green color as it runs from the cells. While still liquid it is bailed into the cast-iron drums in which it is sold.

The good features of the process are the high output per cell, many times larger than that possible with any wet process cell of similar size, the saving of the expense of boiling down weak caustic liquor and of dissolving salt, etc. The drawbacks are the somewhat high voltage necessary and the dilution of the chlorine which is drawn off, mixed with about 20 or 30 times its volume of air. This weak chlorine is well adapted for certain purposes, but not all. Its use in manufacturing bleaching powder necessitates the use of mechanical absorbers.

The anodes withstand the chemical action of the chlorine remarkably well, but are somewhat liable to mechanical injury from careless handling. The furnace castings have a life of seven or eight months under favorable conditions, but are liable to be cracked at the time of starting or shutting down, unless this is done very gradually.

The electrolysis of fused salt proceeds best at temperatures not greatly exceeding its melting-point. At higher temperatures a mist, supposed to consist of subchloride Na_2Cl, diffuses upward from the cathode, reducing the current efficiency very greatly.

Aschcroft Cell. Ashcroft has also devised a cell for electrolysis of fused common salt. His cathode of fused lead is circulated by the action of a powerful electromagnet. The lead sodium alloy is withdrawn and is made the anode in a second cell. After plating out its sodium content as metal in a bath of caustic soda, the lead is returned to the primary cell.

Chlorine is also produced by the electrolysis of fused zinc chloride which melts at a low temperature. Carbon anodes and a cathode of fused zinc are generally used. The process has been in successful operation in England for a number of years and forms an important feature of the Swinbourne and Ashcroft process of treating complex ores. It is necessary to keep the zinc chloride entirely free from oxide. In this point lies the chief difficulty of the process.

Electrolysis of Aqueous Salt Solution.—The reactions occurring in the electrolysis of an aqueous solution of salt are very complicated. On passing a current between insoluble electrodes the primary action is of course the liberation of chlorine at the anode and sodium at the cathode. The chlorine escapes from the system chiefly as a gas, but a small portion dissolves in the electrolyte and begins to diffuse toward the cathode. The sodium liberated at the cathode immediately combines with water, forming caustic soda and liberating hydrogen as a gas.

$$Na+H_2O=NaOH+H.$$

The caustic soda immediately begins to diffuse toward the anode. As soon as chlorine from the anode and sodium hydroxide from the cathode meet, hypochlorites are formed.

$$2NaOH+2Cl=NaOCl+NaCl+H_2O.$$

The action is further complicated by the caustic soda and sodium hypochlorite both beginning to carry current, and electrolyzing:

$$2NaOH=2Na+2OH.$$

The hydroxyl ions discharge at the anode, forming water and oxygen, which escape with the chlorine or act upon the anode material and dissolved products about the anode. The hypochlorite is likewise decomposed and the formation of chlorate in the electrolyte begins. This again carries current. If no means be provided to keep the anode and cathode products

separate, the current efficiency, which was at the beginning 100 per cent, drops to a very low figure. In the direct formation of hypochlorites and chlorates by electrolysis the combination of the anode and cathode products are essential, but in the production of sodium hydroxide and chlorine this must be, as far as possible, prevented. This has been achieved by a variety of means giving rise to a number of successful but very different processes. The necessity of obtaining caustic soda of as high a concentration as possible has also had its influence in the types of apparatus devised. The reaction:

$$NaCl+H_2O=NaOH+H+Cl,$$

represents an expenditure of energy equal to 53 cals. By simple calculation the critical or theoretical minimum voltage is found to be 2.29 volts, much lower, therefore, than the critical voltage for fused salt.

According to the means adopted to prevent or minimize the interaction between the primary anode and the cathode products, the processes may be divided into three classes:

A—Mercury cathode;
B—Diaphragm;
C—Bell type.

Castner-Kellner Process. This may be considered as the type of mercury cathode processes, of which it is the oldest and most generally successful example.

The Castner cell, Fig. 159, consists of a slate box 4 ft. long, 6 ins. deep and 4 ft. wide, divided into three compartments by partitions extending to

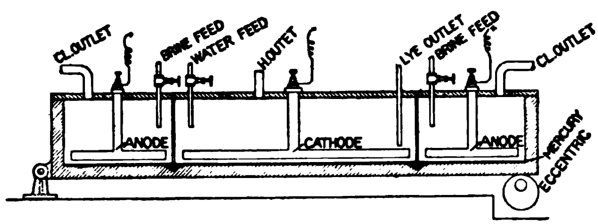

FIG. 159.

within $\frac{1}{16}$ of an inch of the bottom. These compartments are kept separate by a layer of mercury covering the entire bottom of the apparatus. The outer compartments are filled with strong salt solution and the center compartment with pure water. In each outer compartment there are several T-shaped anodes of Acheson graphite, having the lower surface within one inch of the mercury. In the center compartment is an iron grid which serves as the cathode. The cell is pivoted on one end and rests on an eccentric on the other, which raises and lowers $\frac{1}{2}$ in. once a minute, imparting a rocking motion and causing the mercury to flow backward and forward between the compartments. On passing the current the salt in the outer compartments is decomposed, liberating chlorine at the anodes, which is

drawn off by slight suction. Sodium is liberated at the intermediate cathode of mercury and alloys with it. The sodium mercury alloy flows into the center compartment, where it plates out sodium at the iron cathode. The sodium instantly combines with the water, forming caustic soda and hydrogen. The caustic soda dissolves while the hydrogen is allowed to escape into the room. Part of the current must be shunted off before passing to the final iron cathode. Only 90 per cent of the charging current is allowed to pass through the discharging cell, otherwise mercury would pass into solution in the cathode compartment, forming HgO, destroying the continuity and clean metallic liquid character of the mercury and causing a heavy loss of this expensive material.

The salt solution flows through the anode compartment continuously, being brought back to its original high concentration by the addition of salt outside the cell and then returned for reuse. As the sulphates in the brine accumulate, they are from time to time removed by precipitation with barium chloride. The water in the center compartment is left until the caustic soda has raised its gravity to 1.3. The caustic soda solution is then run off and replaced by fresh water. The lye is boiled down in cast iron pots till anhydrous, and is packed molten into iron drums. It is very pure, often 99 per cent actual sodium hydroxide.

The cells are inexpensive to construct and last indefinitely, likewise the iron cathodes. The anodes last a year or more. The current at the anode is about 630 amperes per cell, of which 10 per cent is shunted off before discharging in the cathode compartment. The voltage is about 4.3. The current efficiency is nearly 90 per cent, energy efficiency 47 per cent. The current density at the anode is about 150 amperes per square foot, and at the mercury 110 amperes per square foot. The current which can be used is limited by the necessity of keeping the temperature of the cell below 40° C., at which point chlorate begins to form. Each cell decomposes per twenty-four hours, 65 lbs. sodium chloride, forming 44 lbs. sodium hydroxide and liberating 39.4 lbs. chlorine. The output per H.P. per twenty-four hours is 12.0 lbs. sodium hydroxide and 10.8 lbs. chlorine.

The two factors which have most largely contributed to the success of this type of cell are:

(1) The rocking mercury cathode.

(2) The cathode shunt.

Each Castner cell requires about 150 lbs. of mercury, which it is essential to keep bright and clean, and of which there must be no loss. The mercury is not dissolved by the brine as long as it is electrically negative and does not oxidize in the center compartment unless denuded of sodium; hence the necessity of a higher charging than discharging current.

Whiting Cell. A cell of a somewhat similar kind is that of Whiting, in operation at Rumford Falls, Me. Here the mercury is circulated by means of a pump, and the decomposing compartment is not in electrical contact, i.e., mercury-sodium is formed and is removed from the system

mechanically, decomposed outside the circuit and the denuded mercury returned. The voltage is somewhat higher than that of the Castner cell. The current efficiency is high.

Diaphragm Processes. In cells of this type the anode and cathode are separated by a porous partition, which in most successful cells is in close contact with the cathode. Concentrated salt solution is usually fed into the anode compartment and flows toward the cathode under slight head. The diaphragm controls and regulates the forward motion of the salt solution and retards the backward flow of the caustic soda formed at the cathode. The caustic liquor formed at the cathode is drawn off continually. If the rate of flow is high the crude cathode liquor contains much salt, and the percentage of sodium hydroxide is low; if the flow is slower the concentration in sodium hydroxide will be higher and the lye will contain less salt, but there will be greater diffusion of sodium hydroxide backward through the anode compartment, with recombination, etc., and loss in electrical efficiency.

MacDonald Cell. A simple cell of this type is the MacDonald. This cell consists of an iron tank 1 ft. wide, 1 ft. high, and 5 ft. 2 ins. long, divided into three compartments by two perforated iron partition walls, having five $\frac{1}{32}$-in. holes per square inch. These perforated walls are the cathodes. The diaphragm is stretched upon the inner surface of these walls and consists of a layer of asbestos paper cemented to a layer of asbestos cloth by means of silicate of soda. The anodes of graphitized carbon connected in multiple are suspended in the inner compartment, connection being made through the iron cover which seals the anode compartment. This cover is protected from the action of the chlorine here liberated by a coat of cement. Brine is fed in automatically and continually in the center compartment, and weak caustic soda solution flows off from the cathode compartments. The chlorine is withdrawn from the anode compartment by a slight suction. The voltage is about 4.5, current 420 amperes, output in chlorine 28 lbs. per twenty-four hours per cell, or 10.4 lbs. per H.P. per twenty-four hours.

Hargreaves-Bird Process. In the Hargreaves-Bird process the caustic is converted to carbonate at the cathode and its backward diffusion thus prevented. The cell, which is shown in cross-section, Fig. 160, consists of a cast-iron box 10 ft. long, 5 ft. high, and 2 ft. wide. The cathodes

FIG. 160.

of copper gauze support the diaphragm of an asbestos, silicate of soda, Portland cement composition, and divide the cell into three compartments. The inner compartment contains the anodes of retort carbon, with lead connections which are protected by a coat of cement. The diaphragm is sufficiently impervious to prevent the brine with which the inner compartment is filled to flow through, en masse, but permits electrolysis to take place through it. The space between the outer cathode walls and the walls of the cell is empty of liquid. In it a mixture of steam and carbon dioxide is blown which forms carbonate of soda solution on the walls of the cathode which trickles away. The chlorine liberated at the anode is pumped out of the anode compartment, along with the brine, the chlorine is trapped off, the brine brought back to its original concentration by saturating with more salt and returned by a stoneware pump to the cell. The current in the Hargreaves-Bird cell is high, voltage low, 3.3 volts, but it labors under the disadvantage of producing low-priced sodium carbonate instead of the more valuable sodium hydroxide. The output per cell per twenty-four hours is, sodium carbonate 170 lbs., chlorine 113 lbs., per H.P. per twenty-four hours, sodium carbonate 18 lbs., chlorine 12 lbs.

Townsend Cell. In the Townsend cell the anodes are of graphite, the cathodes are perforated iron plates, separated from the anode compartment by vertical diaphragms which adhere closely to the iron cathodes. The outer surfaces of the cathode plates are bathed in kerosene in the cathode compartments. The anode compartment is kept filled with brine. A hydrostatic pressure is maintained whereby a portion of the brine flows slowly from the anode into the cathode compartments. As soon as current is passing, this escaping brine is charged with the caustic soda formed by electrolysis. Passing through the perforated iron plates it meets the kerosene bath and forms oily drops which detach from the walls and sink to the bottom of the kerosene, out of electrical or chemical contact with the system, and is continuously removed. The spent anode brine is pumped continuously from the anode compartment to a tank where it is saturated with salt and the chlorine trapped off. It is then returned to the cell. The cells are made in rather large units and carry from 4000 to 6000 amperes per cell. The composition of the cathode liquor varies with the rate of percolation. With the rate found most advantageous in practice the composition is about 150 grams sodium hydroxide and 213 grams sodium chloride per liter, with lower hydrostatic pressure and reduced percolation—the composition can be brought to sodium hydroxide 250 grams, sodium chlorid 140 grams. This cell can be run at very low voltage, as low as 3.5, with a current density of 70 amperes per square foot at the anode, but with increased current density (140 amperes per square foot at the anode), the voltage rises to about 4.7. While the yield of sodium chloride and chlorine per H.P. is less at the high density the output per cell is greater, and it has been found on the

whole more economical to sacrifice power to greater output per unit of plant.

Baekland Diaphragm. The diaphragm, which is the invention of Dr. Baekland, consists of asbestos cloth filled with a special paint made of a mixture of oxide of iron, asbestos fiber and gummy iron hydroxide. The diaphragms become clogged in five or six weeks so are removed and given a fresh coat of the paint. This diaphragm is very economical and efficient.

In all the diaphragm processes the primary cathode products consist of a solution of caustic soda and salt. This is boiled down in cast-iron vessels, usually under a vacuum with triple or quadruple effect. At a moderate concentration most of the salt separates out, the caustic soda remaining in solution. The salt is removed (fished), and after neutralizing the small amount of entrained caustic with hydrochloric acid, goes back into the process.

The anode liquor is very destructive to carbon or graphite electrodes if it becomes alkaline; this is guarded against, in some processes, by the addition of a little hydrochloric acid at the anodes. Other diaphragm processes which space does not permit the description of are the Roberts, using a diaphragm compounded of anthracite coal, the Leseur, the Outheu-Chalandre, etc.

Bell Process. In the bell processes, of which there are several, combination of the anode and cathode products is prevented without the use of a diaphragm by suspending the anodes in bells, admitting the brine at the anode at such a rate that it flows past the cathode faster than the cathode products can diffuse upward. The apparatus is very simple, but current density is low and the size of the cells is small. The cathode liquor is very weak in caustic soda and very high in salt, necessitating boiling down a great quantity of liquid. In Aussig and other parts of the continent of Europe, where fuel and labor are cheap, it has, notwithstanding, been commercially successful. A simple type of cell is shown in Fig. 161.

FIG. 161.

A, bell with chlorine outlet tube, and trapped brine feed pipe; *B*, anode of retort carbon; *C*, cathode of iron gauze; *D*, overflow syphon for cathode liquor.

Platinum anodes have been successfully used in the electrolysis of salt, the chief objection is their high original cost. There is some gradual loss of platinum, but in a properly designed plant the expense need not exceed nine or ten cents per 100 lbs. chlorine produced.

The following balance sheet shows the cost per twenty-four hours of a plant producing 12,670 lbs. sodium hydroxid and 12,500 lbs. chlorine, using one of the diaphragm processes:

Balance Sheet

Power-cells, 1200 H.P., at $17 per horse-power year	$55.89
Power-motors, 25 H.P., at $17 per horse-power year	1.16
Salt, 23,000 lbs. at $4.50 per ton	51.75
Superintendence	20.00
Labor, 14 men, at $2.25	31.50
Coal, 8 tons, at $3.50	28.00
Depreciation and taxes	23.95
Maintenance and repairs	31.25
Drums, 27, at 91c	24.57
Debit	$268.07
Credit.	
12,500 lbs. chlorine, at .01 .... $125.00	
Cost of 12,670 lbs. caustic soda	$143.07

Chemical Processes. Of the purely chemical processes for preparing chlorine two survive, the Weldon and the Deacon process. Both use muriatic acid as the source of chlorine. Because of the expense incident to transporting this acid, wherever chlorine is produced in a large way chemically, the acid is made on the spot.

Weldon Process. Muriatic acid is oxidized by manganese dioxide, liberating chlorine at a moderate temperature.

$$MnO_2+4HCl=MnCl_2+2H_2O+Cl_2.$$

The primary source of the dioxide is the mineral pyrolusite, which contains from 50 to 70 per cent of manganese dioxide. High manganese dioxide content is very desirable for chlorine manufacture, and less than 57 per cent renders the mineral unsuitable for the purpose. The muriatic acid should be of high concentration, 30 per cent upward of actual hydrochloric acid and fairly free from sulphuric acid, otherwise the regeneration of the manganese dioxide becomes difficult or impossible and the process unprofitable. The generation of chlorine is always conducted in stone ware stills (fire-brick, sandstone), etc., which may be of rather variable design. In starting with pyrolusite, the mineral is placed in the still first, on a raised platform, then the acid, preferably warm, is run in gradually, finally the still is moderately heated by blowing in a current of live steam. The muriatic acid acts on the dioixde until its concentration is reduced to about 5 per cent actual hydrochloric acid. With recovered manganese the acid is utilized down to about 2 per cent. The chlorine is evolved in a steady stream and is conducted by lead or stoneware pipes to the point of utilization. Since pyrolusite is fairly expensive, the profitable production of

chlorine necessitates the recovery of the manganese from the spent still liquor. The Weldon process, which is the most successful method of doing this, is based on the fact that freshly precipitated manganous hydroxide suspended in a solution of calcium chloride is easily converted into peroxide by a current of air forced through the liquid, if there be present an excess of lime. The excess of lime is essential.

Process of Recovery. The spent liquor from the still is run into a neutralizing well, where it is treated with ground chalk, or better with regenerated manganese mud. The free hydrochloric acid is thus neutralized, and any iron present is precipitated. The residual chlorine dissolved in the liquor is carried off along with the evolved carbon dioxide to a tall chimney, whence it escapes, or it may be removed by passing through a scrubbing tower.

The neutralized liquor is allowed to settle for a few hours, when the clear solution is run into the oxidizers. These are iron tanks 10 ft. in diameter and 30 ft. high, with a perforated pipe at the bottom through which air is admitted under pressure.

The oxidizer is about half filled with manganese liquor (averaging 60 grams per liter manganese as manganese dioxide). By means of live steam the liquid is heated to 55° C. Lime water, prepared by slaking pure lime very low in magnesium, is then run in till all the manganese is precipitated as manganous hydroxide. Then $\frac{1}{4}$ to $\frac{1}{3}$ excess is added. Meanwhile the air is blowing full blast through the liquor. The liquor is at first yellow but gradually becomes black. The first blowing is continued three to five hours, till the liquor, which was at first strongly alkaline, is nearly neutralized and no more manganese dioxide forms.

About $\frac{1}{4}$ as much manganese liquor as originally used is then added, and blowing is continued for another two hours.

The mud is then run into settlers, where it remains until the precipitate subsides. The clear supernatant solution of calcium chloride is then run off as a waste.

The current of air must be very powerful, otherwise what is known as a stiff batch is liable to form. If there is not sufficient excess of lime the oxidation is only partial and what is known as a red batch is formed. This consists chiefly of Mn_3O_4.

About 168 cu.ft. of air are required to produce 1 lb. of manganese dioxide.

The use of recovered manganese mud greatly simplifies the production of chlorine. Very much larger stills, usually pentagonal, are used. Muriatic acid is run into the still about 2 ft. deep, then gradually manganese mud is admitted until an even current of chlorine is produced. Finally, to utilize the last of the acid and drive off the dissolved chlorine, steam is blown in. The spent liquor then goes back to the recovery plant.

The reactions which occur in recovery are about as follows:

I. $100MnCl_2+160CaO=100MnO+60CaO+100CaCl_2$.
II. $100MnO+60CaO+86O=48CaO.MnO_2+14MnO.MnO_2+12CaO.2MnO_2$.
III. $48CaO.MnO_2+24MnCl_2=24CaO.2MnO_2+24MnO+24CaCl_2$.
IV. $24MnO+12O=12MnO.MnO_2$.

From $124MnCl_2$ (original 100 and second addition of 24) there are produced 98 MnO_2 (along with 36 CaO and 26 MnO).

Deacon Process. The Deacon process is based on the oxidation of gaseous hydrochloric acid by the oxygen of the air in the presence of a suitable catalyzer.

$$2HCl+O=H_2O+Cl_2.$$

The catalyzer most used is copper chloride, which functionates as follows:

(1) $2CuCl_2=Cu_2Cl_2+Cl_2$;
(2) $Cu_2Cl_2+O_2=2CuO+Cl_2$;
(3) $2CuO+4HCl=2CuCl_2+2H_2O$.

This reaction begins at 250° C. and reaches its maximum at 400°C. The rate of action of the catalyzer depends upon the surface exposed more than on the amount, and therefore the catalyzer used in practice is broken bricks or burnt clay balls which have been soaked in copper solution (3 per cent) and dried. The reaction is slightly exotherinic, but heat must be supplied to make up for the loss by radiation, etc. In practice about 60 per cent of the hydrochloric acid is decomposed, but the rest is recovered as weak acid. The catalyzer soon loses its activity from a variety of causes, principal of which seem to be the presence of sulphuric acid and arsenic.

The gases, hydrochloric acid, air and moisture, from the decomposition of salt by sulphuric acid in an ordinary salt cake furnace, are cooled by passing through long glass pipes and a small tower filled with coke to remove moisture. They next pass to an iron preheater, where they are heated to 400° C. (hot, dry hydrochloric acid has little action on iron). The hot gaseous mixture then passes through the decomposer filled with the contact substance, the temperature of which is carefully regulated. The decomposition is here affected, the escaping gases being chlorine, water in the form of steam, hydrochloric acid, nitrogen, and a little oxygen.

The gaseous mixture is first cooled by passing through a long series of pipes. The hydrochloric acid is next removed by washing with water in a scrubbing tower, and is finally dried by washing with sulphuric acid in a lead-lined tower. The contact substance is removed every two weeks, one-sixth at a time, thus each portion remains in service twelve weeks.

The Deacon process produces chlorine of about 5 to 8 per cent volume concentration. This is its chief drawback. It produces chlorine more

cheaply that the Weldon process, but the plant is expensive and there have been few new Deacon installations since the advent of the newer electrolytic processes.

In the Weldon process about 35 per cent of the hydrochloric acid is converted to chlorine, the rest to waste calcium chloride. In the Deacon process about 60 per cent is converted and the rest recovered.

Hypochlorites. Chlorine being a gas, does not admit of easy transportation as such. It may be liquefied by combined cooling and pressure, and can then be shipped under pressure in iron cylinders, which latter are not acted upon by dry liquid chlorine.

Chlorine combines with aqueous solutions of the alkaline and alkaline earth hydrates, or with the hydrates in the presence of moisture forming hypochlorites.

$$2NaOH+Cl_2=NaOCl+NaCl+H_2O.$$

The hypochlorites are very powerful bleaching and oxidizing agents. Calcium hypochlorite is the cheapest powerful oxidizing agent that we have. Their value depends in most cases upon the ease with which they give up oxygen to oxidizable organic matter, rather than to any action of the contained chlorine.

$$Ca(OCl)_2=CaCl_2+O_2.$$

Aqueous solutions of hypochlorites are produced in large quantities for use at the place of manufacture. Because of their bulk (it is difficult to prepare hypochlorite solutions much over 130 grams hypochlorite per liter) and instability, such solutions are seldom transported. Occasionally bleach liquor (calcium hypochlorite solution) is shipped a few hundred miles in tank cars if it can be used immediately.

Sodium and potassium hypochlorite solutions (Eau de Javelle, Labarraque solution) are made to some extent by the direct action of chlorine gas upon solutions of the respective alkali hydrates for use in laundry work, bleaching and disinfecting. They are more commonly produced from calcium hypochlorite by double decomposition.

$$Ca(OCl)_2+Na_2CO_3=2NaOCl+CaCO_3.$$

Calcium hypochlorite is cheaper and equally good for many purposes. It is made by absorbing chlorine in milk of lime, which takes it up with great avidity. The manufacture is very simple. It is merely necessary to keep the lime in excess throughout and to keep the temperature below 35° C. If the chlorine gets in excess, or the temperature above 37° C., rapid decomposition and formation of chlorate begins. The presence of iron likewise tends to cause decomposition, particularly if there be little excess of lime. In the manufacture of bleach liquor it is preferable to dilute the chlorine with air as the danger of local over-

heating is thereby greatly reduced. The apparatus in which bleach liquor is made and stored is commonly constructed, or at least lined with Portland cement concrete, which is not acted upon and answers the purpose admirably. Fig. 162 shows a very good type of bleach liquor machine in section. A mixture of lime and water meets a stream of chlorine on the counter-current principle, is elevated by a centrifugal pump, more lime is added and the operation is repeated till the entire charge is up to the desired strength, the operation being entirely continuous and automatic except as regards the addition of lime.

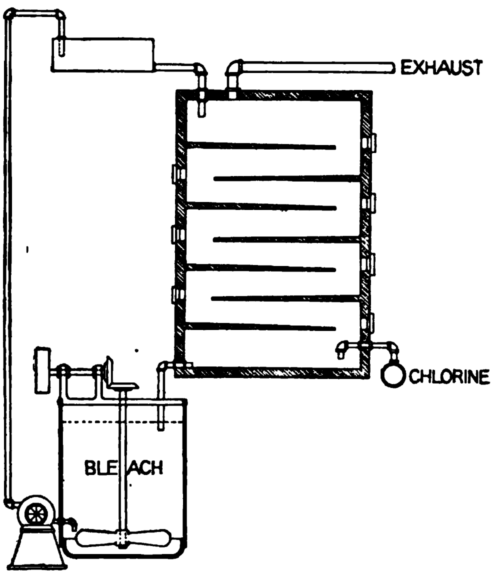

FIG. 162.

Although calcium hypochlorite is almost always used in solution, it is commonly manufactured for sale in the solid condition which is more stable and more easily transported. Slaked lime $Ca(OH)_2$, containing a slight excess of water (2 to 5 per cent) readily takes up chlorine forming bleaching powder which has the composition,

$$CaO.CaOCl_2+2H_2O.$$

The CaO in the best bleaching powder amounts to about 10 per cent Bleaching powder is readily soluble in water; the excess lime forming a sediment:

$$2CaOCl_2+H_2O=Ca(OCl)_2+CaCl_2+H_2O.$$

In making bleaching powder burnt lime low in magnesia and carbonic acid is first slaked so as to contain about 26 per cent water. It is then carefully sifted through iron screens and allowed to cool completely. It is then spread in a thin layer 3 or 4 ins. deep on the floor of a so-called "chamber," a room usually about 6½ ft. high. Chlorine gas is then admitted through the roof and slowly passes to another chamber in series after the lime in the first chamber has taken up most of the chlorine. It usually takes about twenty-four hours for the lime to become completely saturated. In case lime deeper than 2 ins. is placed on the floor, it becomes necessary to interrupt the gassing and for workers to enter the chamber and turn the lime with a spade. Finally the bleach is shoveled

into wooden casks or iron drums painted with asphalt paint. The chlorine must be fairly dry and must not be admitted too rapidly. The temperature of the chamber is kept below 45° C. Chlorine diluted with air to about 40 per cent by volume works well. With gas less than 30 per cent chlorine, mechanical absorbers or shelf absorbers with very thin layers of lime must be used instead of chambers. The ordinary bleach chambers are constructed of lead, stone or cement, with usually an asphalt floor. They may be quite large, 30 by 100 ft. is a common size, and must be provided with suitable doors, peep holes, etc. Two hundred square feet of chamber floor is necessary for each ton of bleach produced per week.

Potassium Chlorate. If chlorine acts upon milk of lime at a high temperature (60 to 70° C), the chlorine being in excess, hypochlorite is formed only as an intermediate product, which immediately is converted to chlorate, the final reaction being

$$6Ca(OH)_2+12Cl=Ca(ClO_3)_2+5CaCl_2+6H_2O.$$

This is the reaction upon which the manufacture of chlorate is based. Chlorine is systematically passed over milk of lime in cast-iron cylinders provided with stirrers, which are kept at the proper temperature mainly by the heat which the reaction itself evolves, if the combination is allowed to proceed at a sufficiently rapid rate. The chlorine is passed over the surface of the lime water till most of the lime has dissolved and been converted into chlorate. Any unabsorbed chlorine passes to another fresh cylinder in series where it is utilized. The solution is then boiled down to about 1.35 specific gravity with potassium chloride, which reacts, forming potassium chlorate.

$$Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2.$$

On cooling the bulk of the potassium chlorate crystallizes out. The mother liquors are boiled down a second and third time and strongly cooled to recover the small amount of chlorate which remains in solution. The crude potassium chlorate is purified by recrystallization, and is washed and dried in a centrifugal machine.

Sodium Chlorate. Sodium chlorate is much more soluble than the potassium salt, and cannot be made in quite the same way. In the manufacture of sodium chlorate, calcium chlorate is first made. This is boiled down to about 1.5 gravity and then cooled. Four-fifths of the calcium chloride solidifies. The mother liquor is drained off and most of the calcium precipitated with sodium sulphate, a little sodium carbonate being added to remove the last of the calcium. The solution of sodium chloride and sodium chlorate is then boiled down. Most of the sodium chloride separates from the boiling hot solution and is removed. The solution is then cooled, and much of the sodium chlorate crystallizes out. Twenty per cent or so is, however, left in the mother liquor, which goes back

into process. The separation is based on the greater difference in solubility of sodium chlorate and sodium chloride in hot solutions.

Electrolytic Manufacture of Chlorate. If an alkali chloride solution is electrolyzed and the anode and cathode products allowed to mix as formed, at ordinary temperature alkali hypochochlorites are formed:

$$NaCl = Na + Cl, \quad Na + H_2O = NaOH + H, \quad 2NaOH + Cl_2 = NaOCl + NaCl$$

If the temperature is above 40° C, chlorate is formed:

$$3NaOCl = NaClO_3 + 2NaCl,$$

particularly if the solution is slightly acid. A secondary reaction which occurs is the reduction of chlorate by the hydrogen formed at the cathode.

In actual practice it is customary to electrolyze at a temperature of 70 to 100° C, the heat being produced by using a high current density which also gives a high yield per unit of plant. At this temperature the substances primarily formed at the anode are very destructive to most anode materials. Platinum anodes are least acted upon, and are generally used. The cathode reduction can be largely reduced by the addition of a little calcium hypochlorite to the electrolyte of alkali chloride. This forms a coating of lime on the cathode, and increases the current efficiency greatly.

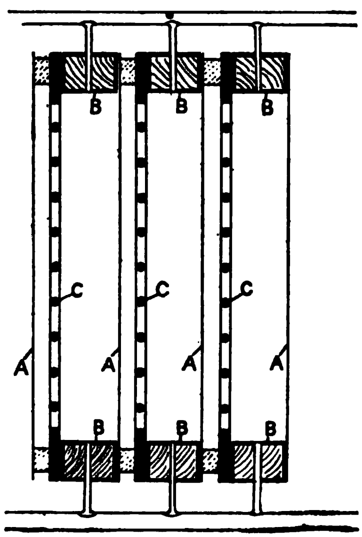

FIG. 163.

The destruction of chlorates during electrolysis may also be reduced by maintaining the electrolyte slightly acid, either by the addition of a little hydrochloric acid periodically, or an acid salt, such as potassium bichromate, which at the same time probably forms a film of chromium oxid on the cathode and reduces the hydrogen reduction. Copper cathodes are generally used.

Gibbs Process. In the Gibbs process, Fig. 163, for the manufacture of potassium chlorate, which has been in very successful operation for a number of years, a solution of potassium chloride containing a little potassium bichromate is passed between anodes of platinum gauze supported on a lead backing, and cathodes of copper in the shape of rods. The distance between anodes and cathodes is only 1-64 inch. The electrodes are kept apart by insulating knobs on the copper rods. The apparatus consists of rectangular wooden frames, alternating with lead plates which support the platinum gauze, packed together in a frame like a filter press, with rubber gaskets between. A great many cells thus occupy only a very

little space, the current passing from one cell to the next in series. The rapid mixture of the primary anode and cathode products is brought about by the hydrogen bubbles formed at the cathode and the rapid circulation of the electrolyte. The chloride solution enters the apparatus at about 20° C., it leaves it at about 70° C., carrying about 3 per cent $KClO_3$. It passes to a refrigerator, where the chlorate crystallizes out, and after resaturation with potassium chloride and adjustment of the free acid goes back into process, the entire operation being continuous and practically automatic. The temperature of the cell is controlled by the rate of flow of the electrolyte.

Owing to the much greater solubility of sodium chlorate, this process is not suitable for its production. In the production of sodium chlorate an electrolyte of salt and a little calcium hypochlorite is used, and electrolysis is continued until the sodium chlorate has reached a concentration of about 700 grams per liter. The electrolyte is kept saturated with sodium chloride throughout.

XII

ELECTROCHEMICAL INDUSTRIES

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By industrial electrochemistry we mean the application of electricity to the manufacture of chemical compounds. The electric current may be utilized in two ways: First, the decomposing effect of a direct current when passed through solutions or molten baths causes a separation of the same into constituents which may be of commercial value as such or else be easily converted into valuable products; second, the current may be used for its heating effect, causing combinations of elements or compounds which cannot be made to take place in ordinary furnaces, or which might suffer contamination if made to take place in such furnaces. We call the first type of operations electrolytic processes and the second type electrothermal processes.

Caustic Soda. By far the most important of the first type of process at the present time is the production of caustic soda from common salt, which has been covered in the previous chapter together with the production of chlorine, hypochlorite, and chlorate.

Pigments. The electrolytic manufacture of pigments has attracted a great deal of attention, but up to the present time has attained no great prominence because of the many unsolved technical difficulties. The production of white lead by the electrolytic dissolution of a lead anode and subsequent precipitation of the basic carbonate has been in commercial use, but is now abandoned. The electrolyte used consisted of a dilute solution of sodium carbonate to which was added a much larger portion of a sodium salt whose acid radicle formed with the lead a soluble compound. Chlorate or nitrate was used for this purpose, it having been found that the use of such a salt in the bath prevented the lead carbonate formed from adhering to the anode and so insulating it. The caustic formed at the cathode of the cell was immediately neutralized by the introduction of a current of carbon dioxide, thus supplying the ingredients used in the process directly as sheet lead anode and gaseous carbon dioxide. The greatest difficulty met with in the commercial operation was the dropping of small pieces of undissolved anode into the deposit of white lead at the bottom of the cell which caused poor color. Another difficulty was the crystalline nature of the deposit at times obtained. More study of the

proper conditions for operating this process must be done to insure its success. Lead chromate can also be obtained in the same manner by using a bath of potassium dichromate and nitrate, regenerating the solution with chromic acid.

The sulphides of cadmium, antimony, etc., have also been made by the use of these metals as anode in a solution of sodium hyposulphite, though the process has never attained much commercial prominence.

Electrothermic Processes

Calcium Carbide. When lime and carbon are mixed together in proper proportions and the mixture heated to an extremely high temperature the lime is reduced and the metallic calcium unites with the excess of carbon present to form the carbide, CaC_2. In general the electric arc is used as the source of heat, though resistance systems have been more or less successfully employed. The reaction which takes place in the furnace is:

$$CaO+3C=CaC_2+CO.$$

This reaction would require a mixture of 875 parts by weight of lime to 563 parts of carbon, though in actual practice the proportion of carbon used for the above quantity of lime rises as high as 650 parts, the excess being consumed in other ways than by the above reaction.

The original carbide furnace consisted merely of a basin into which dipped two electrodes between which an arc was sprung, the reacting mixture being fed directly into the arc. The melting point of the carbide is in the neighborhood of 1800° C, and so the mass sets almost as fast as formed. When the basin was full of set carbide the whole was removed from under the electrodes, allowed to cool and the carbide dug out. The operation was thus an intermittent one, and rather low energy efficiency was attained. A continuous furnace has recently been put into operation with much better results.

Fig. 164 shows one form of this furnace. It consists of a ring mounted on trunnions, so as to revolve in a vertical plane. The whole is made of cast-iron segments bolted together, each piece having its own individual lining of carbon. Hanging down between the two sides is a carbon electrode C forming one terminal of the circuit, the other terminal being the carbon lining of the furnace. The mixture of carbon and lime is fed into an arc sprung between the electrode and the furnace walls. As the carbide is formed the furnace is revolved away from the electrode, making space for more product, cover plates *A* being put on as necessary. As the furnace revolves the material inside cools, and by the time it reaches the

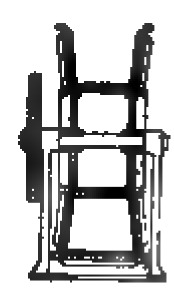

Fig. 164.

side opposite the electrode is so cold that the side and cover plates on this side may be removed and the carbide taken out, the side plates again being reassembled at the top. In this way the furnace can be run continuously. Another form of this furnace uses instead of the carbon lining of the furnace for one of the poles another electrode directed towards the first one, between which the arc is sprung and the material fed. The furnace in use at Niagara Falls is of this latter type. It is 8 ft. in diameter, the outer ring being about 24 ins. deep. It revolves once in twenty-four hours. With an energy consumption of 500 horse-power, one furnace will produce 2 tons of carbide per day. Only about 40 per cent of the heat equivalent of this energy is absorbed in the reactions.

Carborundum. When silica is heated to a very high temperature in contact with an excess of carbon a carbide, SiC, is formed. This is the well-known abrasive called carborundum. The reactions by which it is made may be represented as:

$$SiO_2+3C=SiC+2CO.$$

The arc furnace used in the production of calcium carbide cannot be employed in the manufacture of carborundum, because of the liability of overheating. Although a high temperature is needed for its formation, if that temperature is exceeded metallic silicon will be volatilized from the formed carborundum and graphite will be left behind. It was this accidental discovery that led to the development of the artificial graphite industry to be described later. In practice the carborundum furnace consists of a bed of firebrick 16 ft. long and 5 ft. wide serving as a permanent foundation. The rest of the furnace structure, as the end and side walls, are laid dry and torn down, and replaced with each run of the furnace. The mixture with which the furnace is charged, 3.5 tons of carbon, 6 tons of sand and 1.5 tons of salt is next shoveled on this foundation, carrying up with it the side walls as necessary for its retention. Through the center of this mixture *M*, in Fig. 165, is placed a core of granulated carbon which serves as the resistor, for the development of the electrical heat in the furnace. The ends of this core are in contact with the permanent end connections *E* consisting of carbon bars between which the copper conductors are laid. Such a furnace takes about 1000 horse-power and runs for 36 hours, at the end of which time 3 to 4 tons of commercial carborundum have been made. After such a run the granulated coke forming the heating core has been graphitized, and immediately surrounding and in contact with it is a layer of graphite produced from overheating the carborundum first formed there. Surrounding this graphite is the crystallized carborundum in a layer a foot or more thick, beyond which is found the reduced and

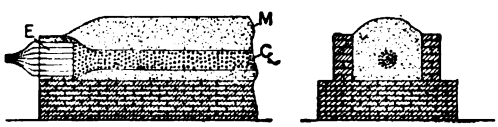

FIG. 165.

uncrystallized carbide, the partially reduced mixture and finally unaltered mixture. The last three products are usually charged back into the next furnace run, though an attempt has been made to utilize the partially reduced material as a refractory. Fig. 166 shows such a furnace in operation, the carbon monoxide being ignited and burning as it issues between the bricks forming the side walls of the furnace.

Artificial Graphite. The overheating of a carborundum furnace led to the discovery that by suitable decomposition of a carbide graphite is left behind. Heating of pure carbon will not transform it into graphite, it

FIG. 166.

having first to pass through the state of a carbide, which requires that some metal or metallic oxide to be mixed with it. In practice, anthracite carrying 8 to 10 per cent ash, uniformly distributed through it, is used for the furnace charge. It may be either moulded into shape first and then graphitized, or else graphitized in powdered form and then used for all purposes of ordinary graphite. It is practically pure, running over 99.5 per cent graphite, all the other impurities having been volatilized at the temperature of the furnace. Fig. 167 shows the furnace used for graphitizing small carbon electrodes. These small electrodes are packed transversely into the furnace, which bears some resemblance to the carborundum fur-

nace. Between the piles of electrodes thin layers of granular carbon are inserted and the whole furnace covered over with carborundum residue. The current is led in through the massive electrodes at the end and traverses both the pile of electrodes and the granular packing. The major portion of the heat is generated in the granular portion of the circuit. Such a furnace is 15 ft. long and consumes 1000 horse-power, the run being about 20 hours. Both the carborundum furnace and the graphite furnace are the invention of Mr. E. G. Acheson, of Niagara Falls, N. Y.

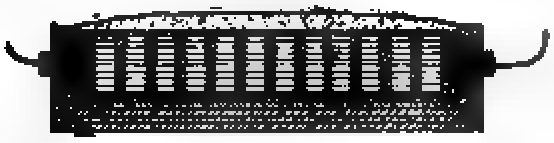

Fig. 167.

Ozone and Nitric Acid. The passage of a current of air through a narrow space between two metallic conductors connected to the terminals of

Fig. 168.

a high tension alternating-current circuit tends to transform the oxygen present into ozone through the medium of the silent electric discharge taking place through the current of air. This ozone is now rapidly making a field of usefulness for itself in the sterilization of drinking water. A plant for the sterilization of 2700 gallons of water per hour by this system is shown in Fig. 168. This plant uses the Siemens and Halske system of generation, the ozone cells being the two rectangular boxes on the top of

the shelf. Each box contains a series of glass tubes lined with tin foil, inside of which is a concentric tube covered with tin foil. Carefully dried air is passed between the two metallic surfaces which are connected with the high-tension circuit.

Fixation of Nitrogen. The passage of a current of air through an electric arc causes the combination of the nitrogen and the oxygen to form one of the oxides of nitrogen, which may readily be converted into nitric acid or into a salt of this acid. But one commercial plant is at present in operation for the manufacture of this acid from air. This is in Norway, and uses the Birkeland-Eyde apparatus. An arc is sprung between special terminals of an alternating-current circuit and forced to take a broad flat form by means of suitable electro-magnets. Through this arc the air is passed. The nitrous oxides are collected in suitable absorbing towers.

It must not be supposed that the preceding processes represent a complete list of electrochemical industries. The application of electricity to industrial chemistry is so recent and competition so active that there are many more applications which are in process of development. The changes in this field are so rapid that what appears standard practice to-day may be obsolete to-morrow. The descriptions, however, of the better developed and applied processes will serve at least to give some ideas of the convenience of the electric current in certain lines of work.

Cyanamide. Nitrogen is absorbed by hot calcium carbide forming what is known in the trade as cyanamide. The reaction involved in the absorption is a reversible one, reading as follows:

$$CaC_2 + N_2 \rightleftarrows CaCN_2 + C.$$

This industry is making rapid strides, there being some fourteen plants in operation throughout the world, the bulk of the product being consumed in the fertilizer industry.

Calcium carbide is first made from lime and carbon by the usual electric furnace process. This carbide is then finely ground and the powdered material charged into a special form of electric furnace where it is kept at 1000°C. Pure dry nitrogen, produced either by the copper oxide or the Linde process is then passed over the hot carbide and is there absorbed. Starting with a carbide containing 75–80 per cent calcium carbide, from 80–90 per cent of the theoretical amount of nitrogen will be absorbed, the resulting product being a grayish-black mass of cyanamide, carbide, and lime. It contains on the average 20 per cent nitrogen.

The American fertilizer manufacturers require that the material be freed from undecomposed carbide and free caustic lime before they can use it. The product is therefore hydrated in specially designed rotary mixing apparatus before appearing upon the market. This hydrated material is sold in the United States under the names *nitrolime* or *lime-nitrogen*.

If cyanamide is treated with superheated steam its nitrogen content is evolved as ammonia, according to the reaction:

$$CaCN_2+3H_2O=CaCO_3+2NH_3.$$

When treated with cold water dicyandiamid is formed:

$$2CaCN_2+4H_2O=2Ca(OH)_2+(CNNH_2)_2.$$

When fused with common salt sodium cyanide is formed. All of these three last described derivatives are becoming of greater importance as a consumer of cyanamide each year.

Iron and Steel. This industry probably represents the largest present development of the electrometallurgical industries. It is treated in detail elsewhere.

Aluminium. It has not proven commercially possible to reduce the oxide of aluminium, Al_2O_3, by heating with carbon. Instead of the metal a carbide is formed. Electrolysis of the oxide dissolved in a melted bath of the double fluoride of aluminium and sodium to which some calcium fluoride is added is used universally in the extraction of this metal. Aluminium as demanded by the trade must be of a high degree of purity, and as the usual impurities, silicon, titanium, and iron are less readily oxidizable than the aluminium itself the usual furnace methods of purification by oxidation are not applicable in the case of this metal. Instead the bath and everything entering into it must be most carefully freed of all foreign elements, so that the metal as extracted will meet the exacting demands of the trade.

The chief source of alumina is bauxite, analyzing

	France.	Arkansas.
Al_2O_3	75.0%	55.59%
SiO_2	1.0	10.13
Fe_2O_3	12.0	6.08
H_2O	12.0	28.99

Three processes may be used for the extraction of the pure alumina from this raw material.

(1) *Fusion Process.* Bauxite is fused in a reverberatory furnace with sodium carbonate forming sodium aluminate. The fused mass is leached with hot water, filtered, the alumina precipitated from the filtrate by carbon dioxide and dried for use in the electrolytic pots.

(2) *Bayer Process.* Finely-ground and lightly-calcined bauxite is agitated with a strong solution of caustic soda in a closed vessel under steam pressure. The alumina passes into solution as sodium aluminate and the impurities remain insoluble. The filtered solution is run off into tall cylindrical vessels provided with stirring apparatus, a small amount of freshly-precipitated alumina is added and the whole stirred. In thirty hours about 70 per cent of the alumina in solution will have

precipitated itself by hydrolysis, the caustic solution being regenerated and ready for use again.

(3) *Hall Process.* Bauxite is fused in an electric furnace with just sufficient carbon to insure reduction of the impurities, silica, titanic acid and ferric oxide. The alumina is not affected. By repeating this operation the product obtained is pure enough for many grades of aluminium.

The fused bath used for dissolving the alumina was originally cryolite, Na_3AlF_6. This has later been modified by the addition of other salts designed to reduce its melting-point and make it lighter in weight. A typical bath consists of $2AlF_3 \cdot 6NaF \cdot 3CaF_2$, though details of the bath composition are kept secret in many plants.

The vessels used for containing the fused bath are rectangular iron boxes 8 ft. long, 4 ft. wide, and about 2 ft. deep, made of sheet steel stiffened by angles. The inside is filled with a baked mixture of tar and carbon from which a cavity is scooped out in the middle for holding the actual fused bath. Above is suspended four rows of ten each carbon electrodes, 3 ins. in diameter, fastened into rods. These electrodes slide up and down, being held to the positive current terminal by screw clamps over the rods.

The bath is fused in the cavity and alumina stirred in. The dissolved alumina is decomposed by the electric current, melted aluminium being plated out on the bottom of the cavity from which it can be tapped as desired. Oxygen appears at the carbon anodes suspended above and consumes part of the carbon to carbon monoxide. The fused fluoride bath itself is not decomposed as long as alumina is added as the bath becomes exhausted.

Such a pot is supplied with 10,000 amperes of current, the resistance offered to the passage of the current serving to supply all the heat necessary to keep it melted. As long as alumina is present in the bath the E.M.F. across the cell varies between 7.5 and 8 volts; as soon as the alumina is exhausted the voltage across the cell rises to 16–20 volts, this rise in voltage being made to actuate a warning signal that the pot needs more alumina stirred into the bath.

Calcium. Calcium is produced by the electrolysis of a fused calcium chloride bath. The calcium is plated out in the solid state and withdrawn from the bath in the form of a rod as fast as isolated.

Sodium and Potassium. These metals are produced by the electrolysis of a fused caustic bath of the corresponding metal. The melted hydrates have great solvent power for the metals and therefore it is necessary to perform the electrolysis within 20° of the melting-point of the hydrate, if a satisfactory current efficiency is to be attained. In the production of sodium the current efficiency is rarely above 45 per cent. The metal is liberated at the cathode, floats to the surface of the bath, and is there drawn off through a trap.

Electrolytic Refining of Impure Metals. *Copper.* Copper as produced by the Bessemerizing of copper matte contains a number of deleterious foreign substances together with silver and gold. Among these substances may be enumerated: Cu_2S, Cu_2O, Au, Ag, Pt, Fe, Ni, Co, As, As_2O_3, Sb, Sb_2O_3, Bi, Bi_2O_3, Se, Te. For economical reasons, it is advisable to separate the precious metals from the copper and the electrical industry requires copper of almost absolute purity, hence some means of refining copper to remove these substances must be used. The most effective means is by electrolytic refining. The crude copper is given a partial refining in a furnace and is then cast into thin flat plates or *anodes* for the electrolytic treatment. These plates are suspended in a bath of copper sulphate and sulphuric acid and a direct current passed from the crude metal plates to others called *cathodes* (see later). Under this treatment the impurities in the anodes behave as follows:

Cu_2S and Cu_2O drop to the bottom as the copper is dissolved out around them and slowly pass into solution. As and As_2O_3 partly dissolve through the action of the current and partly drop to the bottom, slowly passing into solution. Sb and Sb_2O_3 partly pass into solution and partly into insoluble basic salts. Bi and Bi_2O_3 pass into solution and are precipitated out as basic salts. Au, Ag, Pt, Se, Te are not dissolved by the current and drop to the bottom of the tanks as a mud or slime. Fe, Ni and Co pass into solution and are not plated out if copper is present in the solution. Arsenic is not plated out as long as the solution contains free sulphuric acid. In this way we get nothing but copper plated out on the cathode, the impurities either collecting in the slime at the bottom of the tank or in the solution; it is necessary to remove and purify the electrolyte at intervals.

In practice the electrolytes used contain from 10–15 per cent copper sulphate and 5–15 per cent sulphuric acid. Since one ampere of current flowing from an anode to a cathode only plates out or dissolves one ounce of copper in a day and it is not possible with the above electrolytes to use a current density of over 15–20 amperes per square foot of cathode surface without danger of forming rough plating and consequent danger of short circuits, we can readily see that a refinery of any great output must use enormous electrode surfaces. This has led to the development of two systems of connecting the plates up in the electrolytic tanks, the *series* and the *multiple*.

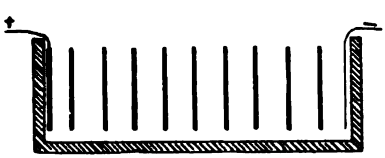

FIG. 169.

In the series system, Fig. 169, a number of copper anodes are suspended in the bath about $\frac{1}{2}$ to $\frac{3}{4}$ in. apart, only the two end ones being connected with the source of current as shown. The current dissolves copper from the first plate and deposits it on the near side of the next plate; the other side of second plate is dissolved and plated out on the

near side of the third plate and so on through the tank. When the anode is nearly consumed it is mechanically separated from the deposit of pure copper on its back. This system is not in very general use, although the largest refinery in the world is equipped with it.

In the multiple system, Fig. 170, the anodes and cathodes are arranged alternately, all the anodes being connected to the positive source of current and the cathodes to the negative. The cathodes are thin sheets of electrically precipitated copper made in special tanks by plating copper on greased lead plates from which it is stripped by hand.

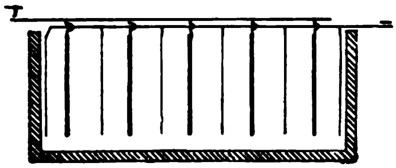

FIG. 170.

Lead. Lead is refined by suspending the impure lead as anode in a bath consisting of 18–20 per cent lead fluo-silicate and 8 per cent fluosilicic acid to which a little gelatine or glue has been added. Lead, zinc, nickel, and iron go into solution and lead and tin only plate out if the solution is kept püre. The impurities for the most part remain as a sponge sticking to the anode.

Silver. For alloys containing above 90 per cent silver with small amounts of copper and gold the electrolyte used is a solution of 2–4 per cent copper nitrate in 1 per cent nitric acid. Silver and copper pass into solution under the influence of the electric current and silver alone is deposited with the low current density of 18 amperes per square foot employed in practice. The gold settles out as a mud in the bottom of the tanks. On account of the silver precipitating on the cathode as loose crystals mechanical means must be taken to prevent crystal-growths from short-circuiting the cell.

Gold. For alloys very high in gold and containing but small amounts of silver and platinum the electrolyte used is a solution of auric chloride in hydrochloric acid. Gold dissolves and is plated out on the cathode, while the silver and platinum remain behind in the slimes.

Nickel and Bismuth. These metals are at present being electrolytically refined by suspending the impure metals as anodes in chloride baths. No details of the processes are available.

XIII

LIME, CEMENT AND PLASTER

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Mortar materials may be classified according to their properties, methods of manufacture and materials from which they are made, as follows:

Common Limes are made by burning relatively pure limestone. When mixed with water they slake and show no hydraulic properties.

Hydraulic Limes are made by burning impure limestone at low temperatures. They slake with water, but show hydraulic properties.

Natural Cements are made by burning impure limestones at a low temperature (insufficient to vitrify). They do not slake with water, but require to be ground in order to convert them into a hydraulic cement.

Portland Cement is made by heating to incipient vitrification an intimate mixture of argillaceous and calcareous substances, which product does not slake with water, but upon grinding forms an energetic hydraulic cement.

Puzzolan Cements are formed by incorporating slaked lime with finely ground slag or volcanic ash or by incorporating Portland cement clinker with suitably treated slag and grinding intimately the mixture.

Plasters are made by heating gypsum sufficiently to drive off three-fourths or all of the combined water, which it contains, and grinding finely the dehydrated residue.

The diagram below will explain the above classifications, while Table I shows the composition of these various materials.

TABLE I.—ANALYSIS OF VARIOUS MORTAR MATERIALS[1]

Material.	From.	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	SO_3	CO_2	H_2O
Lime	Glencoe, Mo.	0.15	0.85		98.01	0.45	....	0.55	....
Lime	York, Pa.	0.52	0.24		97.14	1.28	....	0.96	....
Lime	McNeil, Tex.	0.25	0.15		97.46	0.73	....	1.41	....
Lime	Tiffin, Ohio	1.61	0.17		57.44	40.36	....	0.41	....
Hydrated lime	Union Bridge, Md.	0.38	0.08	0.06	72.59	0.74	....	2.10	23.11
Hydrated lime	Carey, Ohio	0.34	0.18		45.37	31.20	....	3.02	20.07
Hydraulic lime	La Farge Cement	31.10	2.15	4.43	58.38	1.09	0.60	1.28	....
Hydraulic lime	Tiel, France	19.05	0.55	1.60	65.10	0.65	0.30	....	12.45
Plaster of Paris	Nova Scotia	0.11	0.01	0.03	38.90	0.14	54.81	0.54	5.33
Plaster of Paris	Buffalo, N. Y.	2.48	0.32	0.40	37.81	0.39	53.12	0.61	4.98
Natural cement	Cumberand, Md	29.92	4.78	11.23	36.50	11.93	....	5.42	....
Natural cement	Rosendale, N. Y.	27.75	4.28	5.50	35.61	21.18	0.50	4.05	....

[1] From Meade's "Portland Cement."

DIAGRAM OF LIMES AND CEMENTS

Raw Materials.				Classification.
Made from relatively pure limestones.	Burned at low temperatures. 600°–900° C.	Slake on addition of water to burned product.	Not hydraulic.	1. Common limes
Made from argillaceous or impure limestone.				2. Hydraulic limes.
				3. Natural Roman or Rosendale cement.
Made from an intimate mixture of argillaceous and calcareous substances in proper proportions.	Burned at high temperatures. 600°–1200° C.	Do not slake on addition of water, but must be ground finely for use.	Hydraulic.	4. Portland cement.
Made from mixtures of slaked lime and blast-furnace slag or volcanic ash.	Not burned.			5. Slag or puzzolan cements.
Made from gypsum.	Burned at from 165°–200° C.		Not hydraulic	6. Plasters.

TABLE II—ANALYSIS OF MATERIALS USED FOR MANUFACTURE OF LIME AND CEMENT

Material.	From	SiO_2.	Fe_2O_3, Al_2O_3.	CaO.	MgO.	CO_2.	SO_3.	Used for
Limestone...	Annville, Pa.....	0.36	0.45	54.45	0.54	43.24		Portland Cement
Limestone...	Glens Falls, N. Y.	3.30	1.30	52.15	1.58	40.98		"
Limestone...	Mitchell, Ind.....	0.74	0.13	52.94	1.87	43.68		
Marl........	Bronson, Mich...	1.78	1.21	49.55	1.30	40.35		"
Cement Rock	Nazareth, Pa....	13.44	6.60	41.84	1.94	32.94		"
Cement Rock	Martin's Creek, Pa	11.11	6.31	42.51	2.89	36.57		
Clay	Alpena, Mich....	61.09	26.97	2.51	0.65	......	1.42	"
Clay	Suisun, Cal......	58.44	26.50	1.70	1.88	......		"
Cement Rock	Rondout, N. Y...	15.37	11.38	25.50	12.35	34.20		Natural Cement
Limestone, ..	Union Bridge, Md	0.89	0.47	54.68	0.32	43.44		Lime
Limestone...	Woodville, O....	0.78	0.48	31.15	20.78	45.76		"
Oyster Shells.	Long Island Sound	3.30	0.25	52.14	0.25	41.61		"

TABLE III—ANALYSIS OF PORTLAND CEMENTS[1]

Where Made.	Made from	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	SO_3.	Loss.
1 New Jersey...	Cement Rock and limestone	21.82	2.51	8.03	62.19	2.71	1.02	1.05
2 Penna........		21.94	2.37	6.87	60.25	2.78	1.38	3.55
3 Michigan	Marl and clay	22.71	3.54	6.71	62.18	1.12	1.21	1.58
4 Ohio		21.86	2.45	5.91	63.09	1.16	1.59	2.98
5 Virginia......	Limestone and clay	21.31	2.81	6.54	63.01	2.71	1.42	2.01
6 Missouri......		23.12	2.49	6.18	63.47	0.88	1.34	1.81
7 Penna.[2]......		23.56	0.30	5.68	64.12	1.54	1.50	2.92
8 Illinois.......	Blast Furnace slag and limestone..........	22.41	2.51	8.12	62.01	1.68	1.40	1.02
9 Germany.....	....	20.48	3.88	7.28	64.03	1.76	2.46	.....
10 Belgium......	....	23.87	2.27	6.91	64.49	1.04	0.88	.....
11 France.......	....	22.30	3.50	8.50	62.80	0.45	0.70	.....
12 England......	....	19.75	5.01	7.48	61.39	1.28	0.96	.....
13 Germany[3]....	Iron ore and limestone.	20.5	11.0	1.5	63.5	1.5	1.0	.....

[1] From Meade's "Portland Cement." [2] White Portland cement. [3] Sea-water cement.

TABLE IV—AVERAGE CHARACTERISTIC TESTS OF CEMENT IN THE UNITED STATES[1]

Class.	Materials used in Making Cement.	Specific Gravity.	Per Cent Passing through Sieve.		Time of Setting		Tensile Strength in Pounds per Square Inch.								
							Neat.					1 to 3.			
			No. 100.	No. 200.	Initial Min.	Hard Min.	1 Day.	7 Days.	28 Days.	6 Months.	12 Months.	7 Days.	28 Days.	6 Months.	12 Months.
Portland cement	Limestone and cement rock...............	3.14	93.7	75.2	155	392	371	675	750	789	945	239	315	366	442
	Limestone and clay or shale..............	3.13	95.0	76.2	172	341	341	696	825	916	919	252	353	401	403
	Limestone and granulated basic blast furnace slag...........	3.10	98.5	(a)	260	500	358	636	790	888	916	226	298	382	396
	Marl and clay or shale	3.11	94.0	79.2	151	357	328	670	772	780	790	269	352	385	395
	Average.........	3.12	95.3	76.9	185	398	350	669	784	843	893	247	330	384	409
Pussolan or slag cement	Slaked lime and granulated basic blast furnace slag.................	2.88	99.4	95.0	145	452	120	432	502	651	(a)	189	260	272	(a)
												1 to 2			
Natural-rock cement....	Argillaceous limestone ...	2.87	92.6	79.9	34	144	129	197	289	404	501	143	226	295	368

[1] From "Mineral Resources of the United States, Calendar Year 1904."

Lime. *Lime*, when good, is nearly pure calcium oxide, CaO, or a mixture of calcium and magnesium oxides. High calcium limes are stronger than those containing considerable percentages of magnesia. They are also better suited for mortar work, as they slake more readily. Magnesium limes, on the other hand, are better finishing limes, because they work smoother under the trowel. Pure lime, whether magnesium or not, is snow white. A very small percentage, however, of certain impurities

may give the lime a gray or yellow color. These impurities are chiefly iron and manganese. Through certain methods of burning the ash of the fuel may be introduced into the lime, causing discoloration. Wood-burned lime is usually much whiter than lime burned with coal.

Lime is made by burning limestone in suitable furnaces at a temperature sufficient to drive off all of its carbon dioxide, the reaction being $CaCO_3 = CaO + CO_2$. Theoretically, 2350 calories per gram of lime are required to produce this change. This temperature is between 600° and 900° C. If a temperature much above 1200° C. is employed, the lime will be partially fused on the outside of the lumps. This causes the lime to be very slow in slaking, which is undesirable, as some of it may escape hydration in the mortar box and later will expand, or what is technically termed "blow" or "pop" in the wall. This latter manifests itself in small blisters in the finished work.

Intermittent Kilns. The types of kilns ordinarily employed in burning lime may be divided into two classes—intermittent kilns and continuous kilns. The intermittent kilns are primitive and uneconomical. They are, however, frequently used by farmers and other small producers of lime. Fig. 171 shows such a kiln. These kilns are usually made of large blocks of the limestone itself, though sometimes brick is used. The kilns are usually located on the side of a hill in order that the top may be accessible for charging by wagons and the bottom for drawing the lime and supplying the fuel. In charging the kilns an arch of large blocks of limestone is built 2 or 3 ft. from the ground, numerous small openings being left in it through which the flames may pass to the interior of the kiln. The fire is built under the arch, and on the top of the latter the limestone is piled, the charge usually consisting of stone from 2 to 8 ins. in diameter. After the kiln is full, a fire, usually of wood, is started, and the temperature gradually raised to prevent the limestone arch from crumbling. After about six or eight hours the temperature is raised to a red heat and maintained at this temperature for about two days. The kiln and contents are then allowed to cool and the lime drawn by pulling down the arch. There is a great waste of heat and time in these kilns, owing to the fact that the kiln must be cooled and reheated each time it is charged. Old kilns of this sort can usually be seen in any of the limestone farming regions.

Fig. 171.

Continuous Kilns. Three different types of continuous kilns are employed: these are, (1) the vertical kiln with mixed feed, in which the

limestone and fuel are charged in alternate layers. (2) The vertical kiln with separate feed, in which the limestone and fuel are not brought in contact, and (3) the chamber or ring kiln.

Vertical Kilns. Vertical kilns with mixed feed are very similar to intermittent kilns, except that they are provided with an arrangement whereby the lime may be drawn at regular intervals from below. They are also usually somewhat larger than intermittent kilns. Like the latter, they are built on the side of a hill, usually of limestone blocks, and are sometimes lined with firebrick. In charging them, first a layer of anthracite coal or coke and then a layer of limestone is fed into the top. Fire is started at the bottom and works its way up. The process of charging and drawing the lime is continuous. These kilns are economical and, for the same size kiln, yield a larger quantity of product than do the vertical kilns with separate feed. On the other hand, the lime is contaminated by ash of the fuel, and the lime burned in these kilns must be carefully sorted in order to discard those lumps to which the fuel ash has adhered.

FIG. 172.

The vertical kiln with separate feed usually consists of a steel cylinder lined with firebrick. These are equipped with two fireplaces for the burning of the fuel, which are built into the sides of the kiln, so that the fuel is not mixed with the stone. The hot gases of combustion pass from the fire-box into the kiln, while the ash of the fuel drops through the grate bars into an ash pit below, and does not mix with the lime. The kilns are usually constructed with hopper-shaped cooling chamber, set below the fire-box, which is closed by doors at the bottom. The cooling chamber holds about one draw of lime. Fig. 172 shows such a kiln. These kilns are from 6 to 10 ft. in cross-section, and from 40 to 50 ft. in height. They are usually charged by employing an incline and a cable hoist, by means of which the cars of limestone are drawn from the quarry to the top of the kilns. These kilns are sometimes provided with steel stacks in order to induce a better draft, as it has been found that the better the draft the greater facility with which the lime can be burned.

Wood and coal are employed for burning with these kilns. Wood is the best fuel for burning lime, as the wood burns with a longer flame of comparatively low temperature. This is an advantage, as it is essential that the heating should be conducted at a considerable distance inside the kiln without the temperature at the mouth of the fire-box being too high. The steam, which the wood introduces, also seems to be beneficial, and indeed some manufacturers prefer to use green wood because of the greater quantity of steam which it introduces. Wood-burned lime is whiter than that burned with coal.

Where coal is employed as a fuel, it is customary to wet this latter. A steam jet is also often employed, being inserted below the fire-box. The steam passing through the hot bed of coals is decomposed into hydrogen and carbon monoxide as follows: $H_2O+C=H_2+CO$. This gas is burned in the kiln itself, and hence carries the heating zone further into the latter. In order to increase the length of the flame where coal is employed, the Eldred system has been devised and patented. This consists of drawing off part of the spent gas from the top of the kiln and inserting this under the grate bars. This is rich in carbon dioxide, and consequently will not support combustion. The effect is therefore to retard combustion and also to form carbon monoxide by decomposition of the carbon dioxide, as follows: $CO_2+C=2CO$. This carbon monoxide burns in the kiln. Natural gas has also been used as a fuel, and producer gas is now being introduced to some extent. Considerable advantage is claimed for both, owing to the fact that the lime is not discolored by impurities, and also that these gases burn with a longer flame. The use of gas also saves the labor of stoking the grates. These kilns require from 500 to 1000 lbs. of coal per ton of lime produced.

Ring Kiln. The chamber or ring kiln is employed to some extent abroad, but has not been used in this country. It consists of a series of chambers which are built about a central stack and connected to the latter by flues. These chambers are alternately charged with fuel and limestone. Any chamber may be diconnected from the flue at will and also separated from those before and after it by partitions. As a chamber burns out, it is disconnected, the lime removed and the chamber recharged. As a chamber is charged it is connected with the stack and the flames passed through all the other chambers to this one, and thus to the stack. These kilns are economical of fuel, but require considerable labor. (See Chap. IV.)

Hydrated Lime. When lime is treated with water it combines with the water to form calcium hydroxide, $CaO+H_2O=Ca(OH)_2$. If the lime is free from impurities, it will take up 32.1 per cent of its own weight of water. A less amount of water than the theoretical quantity, however, is required to thoroughly hydrate lime, because of the impurities that are always found to a greater or less extent in all commercial limes. Until very recently, lime was always hydrated or slaked by the mason just preparatory to its use. An excess of water was always used, and the cal-

cium hydroxide formed with this a wet mass called lime putty. Recently, mechanical means of hydration have been introduced whereby the lime is hydrated by the manufacturer with just sufficient water to form the hydrate, leaving none in excess. This hydrated lime is a fine dry powder, practically all of which will pass through a 100-mesh screen. It is packed in paper bags or cloth sacks, and will keep indefinitely. It can be stored without danger of causing fire, which is not true of caustic lime. Mortar made with it shows less danger of blowing or popping in the walls. It may be added to cement, when it makes the latter to some extent waterproof and more easy to trowel.

The process of manufacturing hydrated lime is briefly as follows: The lump lime is ground to small size. It is then mixed with just sufficient water, when it falls to a fine powder. The slaked lime is then sieved to separate out the unhydrated lumps or silicious cores from the latter.

The plan adopted in grinding the quicklime in the most successful hydrating plants consists in crushing the lime by means of a "pot" crusher or Sturtevant open-door crusher. This reduces it to pieces about one-half inch and under. Lime which is to be hydrated should not be burned at such a high temperature as is ordinarily used. Fresh lime hydrates much more promptly than that which has been allowed to remain for some time in the air.

There are a number of processes and machines for mixing the lime with water which have been successfully used in hydrating. The two best known of these are the Kritzer and the Clyde hydrators. The latter of these two machines is employed for hydrating magnesian limes with entire success. With high calcium limes, however, the slaking takes place very quickly, and for these the Kritzer machine is now being more extensively used.

The Clyde hydrator is a batch machine, in which a given quantity of lime—usually one ton—is placed. To this is added the proper quantity of water by means of a spray. The machine itself consists of a revolving pan provided with plows which stir up and mix the water and the lime. The water is weighed and added in a predetermined amount. When the operator judges the process to be complete, as is determined by the fluffiness of the powder, the lime is scraped from the pan through an opening in the center of the same into a hopper under the hydrator. It is then ready for the screening.

The Kritzer process is a continuous one. The hydrator consists of a number of cylinders one over the other, which are provided with paddles which revolve around a central shaft. The lime is fed into the upper cylinder in a continuous stream. Here water is spread upon it, the amount being regulated by means of a valve. The moist lime is worked by the paddles and passes through the upper cylinder to the next lower one, etc., and finally works its way out at one end of the bottom cylinder. It is now entirely hydrated and dry. The steam from the lower cylinders passes to

the upper ones, and helps to hydrate the lime. The amount of water to be added in each case is determined by experience. The more calcium oxide the lime contains, the more water must be added.

After slaking, the lime is in the form of a very fluffy powder, all of which will pass through a very fine sieve. It usually contains, however, cores of unslaked lime. These latter constitute the silicious portions of the limestone, which have been partly vitrified, and the over-burned and under-burned lime. They are separated from the hydrated lime by sieving. This is usually done by means of an inclined screen, several forms of which are employed. In one type, the sieve oscillates; in another the wire cloth is covered by small metal bands upon which hammers fall and bounce the material through.

Hydrated lime is now packed in paper and cloth bags. Automatic bagging machines have been devised which allow it to be packed very rapidly in bags, which are pasted shut or tied before the lime is placed in them, this latter being done by means of a valve in one corner of the bags. These paper bags present a square appearance, and not the ragged end of the hand-tied bag.

Hydraulic Lime. Limestones containing appreciable amounts of impurities sufficient to give the calcined product hydraulic properties, but insufficient to take up all the lime present, make, when burned, hydraulic limes. They form an intermediate product between ordinary lime and natural cement. These products range from feebly hydraulic limes to limes which harden quite satisfactorily under water. At one time these limes were manufactured to a large extent in Europe. They have never, however, been manufactured in any quantity in this country. They are made by burning limestone containing from 10 to 17 per cent silica, alumina and iron and from 40 to 45 per cent lime. Magnesia may replace lime to a considerable extent. Hydraulic lime slakes with water just as does ordinary lime, only much more slowly.

Grappier Cements. These are obtained by grinding the hard cores which are obtained in the manufacture of hydraulic lime, and consist of that portion of the hydraulic lime which does not slake when water is added. *La Farge* cement is of this class, and is imported extensively in this country, owing to its light color and the fact that it does not stain marble and other building stones as does Portland cement and natural cement.

Natural Cement. Natural cement was at one time manufactured extensively in this country. Owing to the cheapness, however, with which Portland cement can be manufactured, it is being replaced by this latter. Natural cements are produced by burning and subsequently grinding clayey or argillaceous limestones, which are natural mixtures of calcium carbonate and clay. These limestones usually carry from 13 to 35 per cent clayey matter ($SiO_2+Al_2O_3+Fe_2O_3$), and often a considerable percentage of magnesia, which seems to be interchangeable with lime and to replace the latter without disadvantage.

The kilns used for burning natural cement are very similar to those used for burning lime. The best kiln consists of a steel cylinder lined with firebrick and provided with an opening at the bottom through which the burned material may be drawn from the kiln. The kiln is continuous in operation and the charging is done by introducing at the top alternate layers of limestone and fuel. This latter usually consists of small size anthracite coal or coke. The temperature of burning is usually between 1000° and 1200° C.

After passing through the kilns the burned material presents the appearance of a soft yellowish-brown mass. It is then ground to a fine powder. As it is quite soft, this is usually done with burr-stones or in tube mills. Recently, however, excellent results have been obtained by grinding the natural cements to an extreme degree of fineness by the employment of some of the more modern mills, such as the Fuller-Lehigh Mill. The grinding of the clinker should be at least so fine that 90 per cent will pass through a 100-mesh screen.

Portland Cement. It is now generally agreed that Portland cement is a solid solution of lime in a magma of ortho-silicates and ortho-aluminates of lime. It is therefore impossible to ascribe to Portland cement any definite chemical formula. The composition of Portland cement, however, has a great bearing upon its physical properties. The conditions of manufacture, particularly as to burning and grinding, also influence this. The composition of Portland cement of good quality is usually within the following limits.

COMPOSITION OF PORTLAND CEMENT

	Limits.	Average.
Silica	20–24 %	22.0 %
Iron oxide	2–4 "	2.5 "
Alumina	5–9 "	7.5 "
Lime	60–64.5 "	62.0 "
Magnesia	1–4 "	2.5 "
Sulphur trioxide	1–1.75 "	1.5 "

Practical experience has shown that the essential elements in cement are lime, silica and alumina. Iron oxide is present in nearly all clays and shales, and hence is always present in cement. It has a definite advantage, in that it assists in burning and lowers the temperature of the latter process. Cement containing no iron is white, but rather hard to burn. The proportions of a good cement should satisfy the following ratios.

$$\frac{\text{Per cent lime}}{\text{Per cent silica} + \text{per cent iron oxide} + \text{per cent alumina}} = 1.9 \text{ to } 2.1$$

$$\frac{\text{Per cent silica}}{\text{Per cent alumina}} = 2.5 \text{ to } 4.$$

In the manufacture of Portland cement great care is taken to see that the composition satisfies the above. If too much lime is present the cement will be "unsound"—that is, in time concrete made from it will expand and crack. If too little lime is present the concrete will be low in strength and may "set" quickly—that is, harden before the masons have a chance to place it in the forms. Cement in which alumina is high is also apt to be quick setting, and is hard to burn uniformly. High silica cements are usually very slow hardening, and do not attain their full strength for a considerable period. Cements should not contain more than 4 per cent magnesia, or 1.75 per cent SO_3. The latter is usually introduced in the form of gypsum, and is added to regulate the setting time of the cement.

The materials from which Portland cement is manufactured may be divided into two classes: those which supply the lime and those which supply the silica, iron oxide and alumina. The first are termed calcareous and the second argillaceous. The following groups show the principal materials used in the manufacture of Portland cement.

Calcareous Materials.		Argillaceous Materials.
Limestone	Cement Rock	Clay
Marl		Shale
Chalk		Slate
Alkali waste		Blast furnace slag

The cement rock is an argillaceous limestone which contains usually between 65 and 80 per cent carbonate of lime. If it contains more than 75 per cent it is necessary to add clay, shale or slate to it in order to make a satisfactory mixture for burning. If it contains less than 75 per cent it will be necessary to add limestone for a similar purpose.

Limestone is usually mixed with clay or shale, marls and chalks with clay or shale. Blast furnace slag is used with limestone. Alkali waste (or precipitated $CaCO_3$, obtained from the manufacture of caustic soda) was at one time mixed with clay, but is not now employed for the manufacture of Portland cement.

Limestones, marls and chalks which are to be used in the manufacture of Portland cement should contain less than $2\frac{1}{2}$ per cent magnesia and preferably not more than 3 or 4 per cent silica, iron oxide and alumina combined. Clay, shales and slates should all have at least $2\frac{1}{2}$ and not more than 4 times as much silica as alumina. Exceptions to this are in the case of a high silica limestone, with which a high alumina clay may be used to advantage, since all that is necessary is that the mixture shall satisfy the requirements expressed by the above formulas for the composition of Portland cement.

Three processes are employed for the manufacture of Portland cement—the dry process, a semi-wet process, and a wet process. The dry process is employed exclusively for the manufacture of cement from cement rock

and limestone, and also from limestone and shale and limestone and blast furnace slag. The semi-wet process is employed at a few plants manufacturing cement from limestone and clay. The wet process is employed by plants using marl and clay.

The dry process is an American invention, and is much the more economical of the three. In this process the materials are dried and mixed, ground to such a degree of fineness that at least 92 per cent of the powdered mixture will pass a 100-mesh sieve, and burned at a temperature of approximately 1600° to 1700° C. The resulting clinker is then mixed with 2 to 3 per cent gypsum, and ground so fine that at least 92 per cent will pass the 100-mesh sieve. The resulting product is Portland cement.

In the semi-wet process materials are ground, dried and mixed with a small proportion of water and introduced into the kiln in the form of a wet paste. The resulting clinker is ground with gypsum just as in the dry process. In the wet process the wet marl and clay are ground together without drying, and often, after having more water actually added to them, weighed and introduced into the kilns in the form of a thin mud, called slurry, containing 50 to 60 per cent water, and the clinker ground as before.

Limestone, cement rock and shale are quarried, while clay is taken from beds and marl is dredged from under water. The stone is usually blasted down in benches, an attempt being made to shatter the rock as much as possible. It is then loaded either by steam shovels or by hand into cars and conveyed to the mill. In the dry process the product goes from the quarry to the storehouse, and here it is treated in one of a number of ways. The older method was to dump the product in large piles which were analyzed, and from these analyses the necessary mixture of limestone and clay was calculated. The rock was then loaded on buggies or barrows and wheeled to the crusher after being weighed, where it met another buggy or barrow loaded with the other material to be added. The two barrows were then dumped into the crusher together, one after the other. Another method employed is to weigh the rock as it comes from the quarry and add to the car containing it the proper amount of limestone or clay. This is then dumped into the crusher. In the third system rocks are crushed and even partially ground separately and conveyed into bins, where they remain until the contents of the latter are analyzed. They are then drawn out and mixed in the proper proportions.

The crushing is nearly always done in a gyratory or Gates crusher. The jaw or Blake crusher was at one time used to some extent; but now the Gates crusher, owing to the fact that it has much greater capacity and does not clog as easily, is almost universally used. After being crushed the rock is usually dried. This is done by means of rotary driers. These are cylinders of sheet steel from 4 to 6 ft. in diameter and from 40 to 60 ft. in length. They are unlined, and are usually provided with channel irons bolted to the inside to act as shelves, to carry the rock up and drop

it through the hot gases. The driers are heated by a coal fire at the lower end or else by the waste gases from the rotary kilns. They are similar in construction to the rotary kilns described farther on, except that they are smaller and are not lined with firebrick.

Marl is usually conveyed to the mill by cars, barges or pipe lines in the form of a thin mud. It is passed through some form of pug mill provided with screens which separate out of it any sticks, stones, etc. From the pug mill it passes to large concrete basins or steel tanks, where it is sampled. The clay is usually dried to facilitate chemical work of making a proper mixture, and disintegrated in dry pans. The marl is either measured or weighed, and the proper amount of clay added. From the measuring tank the mixture is pumped into a pug mill and thoroughly mixed. From the pug mill the materials run into large vats, where the mixture is sampled and analyzed, and if not of correct composition more clay is added. The contents of all vats are kept in continual agitation by means of compressed air or mechanical stirrers. When the material has become of correct chemical composition it is passed on for the final grinding, which is done in tube mills.

The grinding of dry materials is usually done in two stages. A number of mills are upon the market for doing this grinding. For the preliminary grinding the ball mill, rolls and the hammer-mill are used, while for final pulverizing the Fuller-Lehigh Mill, the tube mill, the Griffin mill, and the Huntington mill are the ones usually employed. The ball mill consists of a drum filled with steel balls. The drum is lined first with steel plates which lap one over the other to form steps. As the drum revolves the balls fall over the steps, and so pound the material to pieces. The partially crushed material drops through holes in the plates on to perforated steel screens built around the entire circumference of the drum. These screens take out the very coarse particles and return them to the inside of the drum. The finer ones drop on another set of screens made of woven wire cloth, and these separate the fully ground material from the coarse and return the latter back to the mill. The fully ground material falls into a dust-proof casing which entirely surrounds the mill, and then down to the conveyor under the latter, which carries the coarsely ground material on to the next step. The ends of the drum are formed by circular plates, and the material is fed in through a large opening in the center of one of these. The material is fed in by means of automatic feeders, which regulate the quantity of the material admitted to the mill. The size of the product is regulated entirely by the fineness of the last set of screens. When preparing for the tube mill, these are usually 16 to 20 mesh, while if preparing for the Fuller and Griffin mills, all screens are removed. The product of a ball mill equipped with 16-mesh screens will usually, about half of it, pass a 100-mesh screen.

The kominuter is a modification of the ball mill. It consists of a drum about the same diameter as a ball mill, but somewhat longer than the

latter. The kominuter is lined just as is the ball mill, with steel plates which are arranged to lap and form steps. The drum is surrounded by a coarse screen tilting toward the feed end. The material enters through an opening at one end, and is pounded to pieces by the balls. It does not fall out through holes in the plates at once, however, but travels through the full length of the drum, and passes through openings at the opposite end, on to screens. The underground material is returned to the mill by means of *S*-shaped pipes at one end.

The Williams mill consists of hinged hammers which revolve around a horizontal shaft. These crush the material and pass it out through a grid, the bars of the grid serving as part of the crushing surface.

The tube mill consists of a cylinder 20 to 22 ft. long and from 5 ft. to 5½ ft. in diameter, filled with flint pebbles. The cylinder is lined with some hard substance, such as armor plate, chilled iron, quartz, or trap-rock, and revolves at a speed of from 25 to 27 revolutions per minute. The material is fed in through a hollow shaft, and leaves either in the same manner at the opposite end or else through a grating at the perimeter of the end. The flint pebbles are imported from Europe, and the wear on them is not great. Material is usually fed in at a regular rate by means of a screw conveyor operated by means of some form of speed-regulating device. The fineness of the product is controlled entirely by the amount of material fed into it.

Fig. 173.

The Fuller-Lehigh Pulverizer mill, Fig. 173, consists of a horizontal ring or die against which revolve four balls. The balls are propelled by means of pushers. The die and pushers are chilled charcoal iron castings. The balls are of steel forgings. These balls are 12 ins. in diameter, and weigh 260 lbs. each. They revolve at a speed of about 155 R.P.M., and hence press against the die with enormous centrifugal force. The material to be ground is fed into the hopper which serves the feeder. The material discharged by the feeder falls down into the pan of the mill, situated below the die, and is drawn up from this in between the rapidly revolving balls and stationary die by means of air currents induced by fans placed in the chamber above the die. The material is pulverized by the rolling of the balls against the die, the pressure of each ball against the die being over 2700 lbs., the grinding action being similar to that of a mortar and pestle. The finely pulverized material is sucked upwards by means of the fans and out through the screens. The material passing through the screen falls down between this screen and the outer casing, and is discharged

from the mill through the discharge spout, which may be placed at any one of four quarters of the mill. The feed to the mill, and consequently the fineness of the products, may be controlled in two ways: either by a slide on the hopper or by means of the stepped pulley, connected to the screw conveyor by gearing. The mill is provided with two screens one—the inner—of 1-in. mesh and made of very heavy wire to protect the outer one. The outer screen does not really screen, but merely controls the draft of air, and hence the fineness, since the greater the velocity the greater the carrying power of the air, and hence the coarser the product.

The Griffin mill is somewhat similar to the Fuller-Lehigh mill in operation. It consists of a steel die against which a roll also of steel is made to revolve, and it is between these two that the material is ground. The roll is suspended by a shaft from a spider, and actuated by a pulley and a universal joint. The fully ground material is sucked up and forced through the screens. The coarse particles fall back into the pans of the mill and are thrown up between the roll and the die by means of a plow attached to the roll. The finished product passes through the screen and travels from these to the outer casing and thence through openings in the base of the mill to screw conveyors.

The degree of fineness to which the raw material is to be ground depends entirely upon conditions. It is stated as a general rule it should never be ground coarser than 90 per cent through the 100-mesh sieve, and in most cases 95 to 98 per cent is required to produce a sound cement. The finer the grinding the more perfect the combination between the silica, the alumina, the iron and the lime. If the raw materials are not finely enough ground, the cement will be unsound—that is, some of the lime will not combine and will cause the cement to disintegrate.

The material is usually carried from one part of the process to another by mechanical means. Belt conveyors are used for the coarser material and screw conveyors for the finely pulverized. Marl and slurry are pumped through pipe lines, sufficient water being added to make them flow easily.

In the early days of the American Portland cement industry, the burning was done in intermittent upright kilns, similar to those used for burning lime. These were soon improved, so as to economize fuel by making them continuous in action. This allowed the charge to receive the waste heat from the clinkering of the cement, and the air for combustion to be preheated, by passing through the fully-burned material, this serving also to cool the latter. These upright kilns required that the material be moulded into small balls or bricks, which of course necessitated much hand labor. When the material to be burned was not plastic, like a mixture of limestone and clay, it was further necessary to add a binder, such as coal tar or cement itself. About 1887, a rotary kiln was introduced, and this is the form of kiln now universally used in this country, as it allows the material to be fed directly into it, either in the form of a powder or a slurry, thus saving much labor.

Rotary Kiln. The rotary kiln, in its usual form, Fig. 174, consists of a cylinder, from 6 to 8 ft. in diameter and from 60 to 150 ft. long, made of sheet steel and lined with firebrick. The steel sheets are from $\frac{1}{2}$ to $\frac{9}{16}$ in. thick, and are held together by single-strap butt joints. This long cylinder is supported at a very slight pitch ($\frac{3}{4}$ in. to the foot) from the horizontal, on two or more tires made of rolled steel, which in turn revolve on heavy friction rollers. The kiln is driven at a speed of from one turn a minute to a turn in two minutes by a girth-gear situated near its middle, and a train of gears. The power is supplied by either a line shaft or a motor. The upper end of the kiln projects into a brick flue, which is surmounted by a steel stack, also lined with firebrick for its entire height. The flue is provided with a door at the bottom, which serves not only to allow the flue to be cleared of the dust which accumulates in it, but also as a damper to control the draft of the kiln.

FIG. 174.

The material to be burned is usually fed into the kiln through a horizontal water-jacketed screw conveyor, or else spouted into it through an inclined cast-iron pipe. When slurry is to be burned this is pumped into the kiln. The dry raw material is kept in large steel bins above the feeding device, while slurry is stored in vats, in order, in either case, to have on hand a constant and regular supply. The raw material feeding device is usually attached to the driving gear of the kiln, so that when the kiln stops the feed also stops.

The lower end of the kiln is closed by a firebrick hood. This is usually mounted on rollers, so it can be moved away from the kiln when the latter has to be relined. The hood is provided with two openings: one for the entrance and support of the fuel-burning apparatus, and the other for observing the operation, temperature, etc., of the kiln, and through which bars may be inserted to break up the rings of material which form, and to patch and repair the lining. The lower part of the hood is left partly

open. Through this opening the clinker falls out and most of the air for combustion enters.

The kiln is heated by a jet of burning fuel, usually powdered coal, but sometimes (as in Kansas) natural gas and (as in California) fuel oil are used. The coal is blown in by a blast of air supplied by either a fan or air compressor. If the fan is used, about 20 per cent of the air necessary for combustion is supplied this way. If the compressor is employed, only 5 to 10 per cent of the air is delivered by the compressor.

The necessary temperature of the hottest part of the kiln is about 3000° F., and is rarely ever less than 2700° F. To properly maintain this temperature, about 80 lbs. to 160 lbs. of fuel are required per barrel of cement, the actual amount depending on the coal itself, the material to be burned and the dimensions of the kiln. The longer the kiln, the greater economy it will show. Dry materials require much less coal than slurry. With limestone and shale mixture, and a kiln 100 ft. long by 7 ft. in diameter, the coal consumption will amount to about 90 lbs. of good gas slack per barrel. A kiln 60 ft. long by 6 ft. in diameter will, on the other hand, require about 110 lbs. of this material per barrel.

Of the heat supplied to the kiln by the burning of the coal, by far the larger proportion is wasted. About 50 to 75 per cent of it is carried off by the waste gases of the stack, and from 10 to 15 per cent by the hot clinker falling from the lower end of the kiln. The gases enter the stack at from 1500° to 2000° F., and the clinker leaves the kiln at not much under 2000° F. If the kiln could be made to show the same economy as is common in good kiln practice, a barrel of cement could be burned with 25 lbs. of coal.

The raw material as it enters the kiln contains about 33 per cent carbon dioxide. For the first 30 ft. of its journey through a 100-ft. kiln, it is merely heated up, and whatever water it contains is driven off. In the next 40 ft. it loses all its carbon dioxide and sticks together, forming small, soft, lemon-yellow balls, which, as they reach the hottest part of the kiln—the last 30 ft.—partially vitrify, become rough and hard, and turn to a greenish-black color. Properly burned Portland cement clinker is greenish-black in color, of vitreous luster, and, usually, when just cooled, sparkles with little bright glistening specks. It forms in lumps from the size of a walnut to hardly more than dust, with here and there a larger lump. Under-burned clinker is more or less soft, is irregular in shape, and not so black as the well-burned material. Under-burned clinker usually shows soft-brown centers, but hard-brown centers are due to very hard burning.

When coal is used for burning, this is pulverized in mills similar to those used for grinding the raw materials. It is, however, first crushed by passing it through rolls or pot crushers, and then dried in rotary driers of special type. The mills most used for coal pulverizing are the Fuller mill and the tube mill. The latter need not be preceded by a ball mill.

The coal should be pulverized so that 90 per cent of it will pass a sieve having 100 meshes to the linear inch, and should contain from 30 to 45 per cent volatile matter.

Cooler. As the clinker leaves the kiln at about 2000° F., it is entirely too hot to grind, and must be cooled to ordinary air temperatures. This can be done by allowing it to lie in piles; but, as it is a slow way of doing it, mechanical devices are usually resorted to. These may consist of either revolving horizontal cylinders or vertical stationary coolers. The former consist of steel cylinders provided with angle irons on their insides to carry the material up and drop it through the current of air passing through the cylinders. They are mounted on tires and rollers, just as are kilns and driers, and revolve at a speed of about a turn or two a minute. They are usually placed below the kiln, and the clinker falls from the kiln into them. The air for cooling is also drawn through them into the kiln by the draft of the latter. They thus serve not only to cool the clinker, but also to preheat the air entering the kiln.

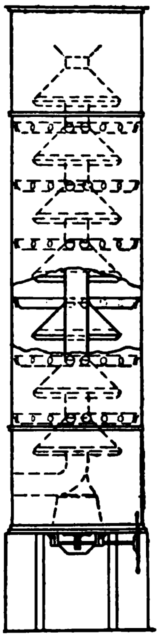


FIG. 175.

The upright cooler, shown in Fig. 175, is almost universally used in the Lehigh district. It consists of an upright steel cylinder, 8 ft. in diameter and 35 ft. high, provided with baffle plates and shelves. As the clinker falls over these, it meets a current of air blown in through a perforated pipe running up through the center of the cylinder, and is thus cooled. The clinker is carried from the kiln into these latter coolers by means of bucket elevators, water being run into the buckets to keep them cool. This also suddenly chills the clinker and makes it brittle and easier to grind.

After cooling, the clinker is ground in Fuller mills, Griffin mills or ball and tube mills. In the case of the Fuller and Griffin mills, it is usually found more economical to crush the clinker down to pea size by a set of rolls, before feeding to the mills. Kent mills and air separators, and also Kent mills which grind as preparation for the other mills, are used to a limited extent. The clinker should be ground so fine that at least 92 per cent of it passes a sieve having 100 meshes to the linear inch.

In order to regulate the set of the cement, since clinker ground alone would set very rapidly, it is necessary to add to it calcium sulphate in some form or other, usually as gypsum, or plaster of Paris. As this can be most easily mixed with the cement during grinding, it is the usual practice to add the retarder to the clinker before the latter is ground, and to grind the two together. The amount of gypsum or plaster of Paris used is usually about 2 or 3 per cent of the weight of the clinker.

After passing through the clinker mills, the cement is conveyed to the

stock house. This usually consists of a long, low building of wood, stone or concrete, cut up into bins. The cement is brought in by an overhead screw-conveyor and dropped into any desired bin by means of a slide in the bottom of the conveyor trough. A screw-conveyor also runs under the floor of the stock house, at the ends of the bins. The latter are provided with removable board ends, and, when it is desired to pack from any bin, these ends are removed and the cement allowed to run into the screw conveyor. When the cement ceases to run, it is necessary to either pull it into the conveyor with a broad-blade hoe, or else to wheel it there in barrows. The screw conveyors then carry it to the packing machines, which are similar to those used in flour mills.

Cement is packed into barrels holding 380 lbs., or into paper or cloth bags holding 95 lbs. each. The cement is packed as shipped, and the bags or barrels are trucked directly to the cars. For this reason the packing-room floor is on a level with the floor of the cars to be loaded, and these latter are brought alongside of the room. A shed roof should run out over the cars, so the loading can be done in stormy weather. Cars usually hold from 100 bbls. to 170 bbls. of cement, with 150 bbls. for an average.

Much more cement is packed in cloth bags than in anything else. In the case of these bags, the consumer is charged with the value of the bag, and credited by a certain amount if the bag is returned in good condition. The bags are all marked with the brand label of the manufacturer, and so each manufacturer knows his own bags. Barrels and paper bags are sold to the customer, and are not returnable.

Plaster of Paris. Plaster of Paris is made from gypsum by heating the latter to a temperature of between 212 and 400° F., when three-quarters of the water of crystallization of the gypsum is driven off, the resulting product being plaster of Paris.

$$2(CaSO_4 2H_2O) = (CaSO_4)_2 H_2O + 3H_2O.$$

In actual practice the temperatures employed to bring about this reaction are 330 to 395° F. If gypsum is heated above 400° F., it loses all of its water of combination and becomes anhydrous sulphate of lime, the latter being the basis of hard finish plaster, floor plaster, Keene's cement, etc.

When plaster of Paris is mixed with water it sets or hardens very promptly, this change being due to absorption of water, forming gypsum again.

$$(CaSO_4)_2 H_2O + 3H_2O = 2CaSO_4 2H_2O.$$

A pure plaster of Paris will normally harden or set in from five to fifteen minutes after having been mixed with water. If the gypsum from which the plaster is made contains impurities, the set will be much slower than this. Plaster to be used for building purposes must be slow setting. For ornamental use, it must also be white; and since the impurities usually

render the plaster slightly colored, it is the common practice to add retarders to the plaster before placing the same upon the market. The materials used as retarders are usually of a colloidal nature, such as glue, sawdust, blood, packing-house tankage, etc. If a very quick-setting plaster is desired, crystallized salts are employed, such as common salt, sodium sulphate, sodium carbonate, etc.

Gypsum, the raw material from which plaster is made, is, when pure, a hydrous sulphate of lime, $CaSO_4 2H_2O$. As mined, however, gypsum usually contains a considerable percentage of impurities, the chief of which are clay, calcium carbonate and magnesium carbonate. The following table gives the analyses of some American gypsums:

Locality.	SiO_2	Fe_2O_3	$CaCO_3$	$MgCO_3$	$CaSO_4$	H_2O
Nova Scotia	0.10	0.02	1.04	trace	78.60	20.13
Kansas	0.35	0.12	0.10	0.25	78.73	20.52
Michigan	1.24	0.50	2.38	....	77.19	19.03
Kansas	2.17	0.24	2.66	0.95	75.11	19.40
Oklahoma	17.95	1.43	....	....	61.00	18.44
Indian Terr.	10.67	0.60	10.21	1.10	59.46	16.59

Impure earthy gypsum, such as that shown in the last two analyses of the above table, is known in the trade as gypsum earth or gypsite.

Gypsum occurs usually in the form of beds, frequently associated with deposits of rock salt, and almost always interstratified with beds of limestone and shale. The beds, of course, vary greatly in extent and thickness, some of them being as thick as 60 ft., while a great many of them are very much smaller than this. The principal gypsum deposits found in this country lie in three geological series—namely, the Salina group of the Silurian, the Lower Carboniferous and the Permian. The localities in this country which produce gypsum are central and western New York, southwest Virginia, northern Ohio, Michigan, and a great many of the western states, Kansas and Oklahoma being large producers.

The usual plan of working the gypsum deposits is by mining, and deposits seldom lie near enough to the surface for quarrying. For the most part the mining methods are crude.

The operation of manufacturing plaster of Paris from gypsum consists in first crushing and grinding the gypsum, then calcining the ground product, and finally pulverizing the calcined product, after which the retarders are added. In some plants, the gypsum is merely crushed and calcined, the calcined rock then being ground very finely. Where the kettle process is employed, the pulverizing, however, is done before the calcining. Where the rotary cylinder process of calcining is used, the pulverizing is done after the calcining.

The process of preparing the gypsum for the kettles usually consists in first crushing it to such a size that it will pass a 2-in. screen. The crushers employed for this purpose are of both the Blake and the Gates types.

The former type is especially devised for cracking gypsum. After the coarse crushers, the gypsum is further reduced by means of a double cone or pot crusher. These crack the gypsum to such a size that most of it will pass a ½-in. ring screen. From the pot crusher the gypsum passes to buhrstones, rock-emery mills, Williams mills or Stedman disintegrators. These reduce the gypsum so that about 60 per cent of it will pass a No. 100 mesh sieve. It is then ready to be fed to the kettles.

Gypsum Kettle. The gypsum kettle consists of a steel cylinder set in brick work. The bottom of the kettle is made of cast iron, and is convex in shape. The bottom has a thickness of about ¾ in. at the edges and 4 in. at the crown. This kettle bottom is a very important part of the apparatus, and is the part which seems to need oftenest repairing. If made from ordinary scrap iron they are apt to crack. Sheet steel has been tried, but does not seem to be as good as the cast iron. A kettle with a sectional cast-iron bottom, which, of course, facilitates repairs, has also been recently employed to advantage. The kettle itself, which is placed on the kettle bottom, is made of boiler iron, ⅜ to ⅝ in. thick. It is from 8 to 10 ft. in diameter and 6 to 8 ft. deep. A kettle of this size will hold from 7 to 12 tons of pulverized gypsum and produce from 5½ to 10 tons of plaster. The kettle is provided with from two to four flues, 12 in. in diameter, placed horizontally about 8 in. above the crown of the kettle bottom, and separated externally about 6 in. The kettle is surrounded by brick work, so that the heated gas from the fire may rise around its sides and through the flues. The top of the kettle is covered with sheet iron, has a movable door and a vent to carry off the water. The two kettles are usually placed side by side and work in pairs.

It is necessary that the material in the kettle be continually agitated. For this purpose the kettle is provided with a stirrer, which is actuated by a vertical pinion wheel and a line shaft. The stirrer itself consists of a cross arm which is curved to conform to the bottom of the kettle and provided with either paddles or a chain which drags along the kettle bottom. The stirrer is run at about 15 to 20 revolutions per minute, and is so arranged as to throw the material towards the center of the kettle. About 15 or 20 horse-power is required to operate the stirrer. If the gypsum is not stirred the charge will settle down and become hard. The bottom would be also immediately melted out of the kettle. In starting a kettle the heat is gradually applied, the crude material is fed in through the charging door and the stirrer put in motion. The material is added gradually until the kettle is full. As the temperature rises, the water begins to be driven off. The mechanically held water is first driven off at a temperature of 212° F., after which the contents of the kettle remain fairly quiet until a temperature of 290° F. is reached, when the material begins to boil and the water of combination begins to be driven off. An expert calciner can tell by the way in which the charge boils when the proc-

ess is finished. When the material has been calcined sufficiently it is run by means of a small grate in the side of the kettle into a pit.

In burning pure gypsum the temperature rarely exceeds 340° F. Thermometers may here be used to advantage. In gypsite plants, however, a higher temperature is required, which may sometimes reach as high as 390° F. Here, owing to the complexity of the material, the proper temperature for calcining varies, and thermometers cannot be used.

The gypsum kettles are arranged in pairs, with a pit to each pair of kettles, in order that the pit may be emptied from one charge while the other is being cooked. The calcined material is carried from the pit, by means of an elevator, to a bolting reel, where the coarse material, usually amounting to only a few per cent, is screened out, sent back to buhrstones and reground. From the bolting reel the material is conveyed to a storage bin. There are usually several of these in order to separate the runs of different days.

Cummer System. The Cummer system of calcining consists in first partially crushing the material, so that it will pass a 1-in. ring screen. The gypsum crushed to this state is fed mechanically into a rotary drier or calciner. The material, in passing through the calciner, is heated to a temperature of from 350° to 400° F., the exact temperature depending upon the nature of the rock. From the drier the gypsum is carried into a storage bin. These bins are built of vitrified brick or concrete, so that they will not take fire or absorb the moisture given off by the gypsum. These bins are also so constructed that the material is thoroughly ventilated. In these bins the calcining is completed, the moisture being driven off by the residual heat of the rock itself. After the gypsum has been partly dehydrated in these bins it is drawn out, crushed, ground, pulverized and bolted.

The retarder is added to the gypsum after this has been finely ground. Usually from 2 to 15 lbs. of the former are required for every ton of plaster. The mixing is done in some form of a mechanical mixer. The Broughton mixer, is extensively used for this purpose. An ordinary wall plaster will also contain, in addition to a retarder, a certain per cent of finely picked hair or other fiber, in the proportion of about 1½ to 3 lbs. of hair to a ton of plaster. Wood fiber is sometimes added as a substitute for hair, and such use is growing.

Plaster is usually packed in jute sacks containing 100 lbs, or in paper bags containing 80 lbs. It is customary in the plaster trade, as in the cement trade, to charge for the jute sacks, and give a rebate on the return of the latter. Where the plaster is packed in paper bags, a charge is usually made for these latter.

Flooring plaster and hard-finished plaster are also gypsum products made by burning this mineral until all of its water of crystallization is driven off. Flooring plasters are prepared by simply burning gypsum at a high temperature, while the hard-finish plasters are produced by a double burning with the intermediate use of some chemical. Practically

all of these plasters are imported. Flooring plasters are manufactured by burning pure gypsum, broken into lumps, in a vertical kiln. The kiln is heated by means of a grate, to one side of the kiln, upon which coal is fired. The hot products of combustion pass through, and so heat the gypsum in the kiln. The temperature reached is about 900° F. The time of burning is four hours. These floor plasters give a very hard and durable surface. They must be very carefully used to prevent cracking.

Of the hard plasters, Keene's is the best known, and was originally manufactured under an English patent. This, however, has long since expired. This cement is not only imported into this country, but is also manufactured to some extent here. It is made by burning a very pure gypsum at a red heat. The resulting anhydrous calcium sulphate is immersed in a bath of alum solution and dried, after which it is again burned at a high temperature, finely ground and placed upon the market. It is necessary to employ a very pure gypsum, as the slightest trace of iron would color the cement.

Puzzolan Cements. Puzzolan cements are of very ancient origin, and in most of the engineering work done by the Romans this cement was employed. They manufactured it by mixing slaked lime with fine volcanic ash. These cements are still employed to some extent in Europe, but have never found a market in this country. A cement manufactured from blast furnace slag and slaked lime was made at one time in this country by a number of concerns, but at the present time its manufacture has been almost entirely discontinued. The activity of this class of cements depends upon the fact that the volcanic ash and slag both contain soluble silicic acid, which readily enters into combination with calcium hydrate to form silicates.

In manufacturing slag cement, the cement is chilled and granulated by running it while still molten into water or by directing a stream of water against a stream of melted slag. This slag is then mixed with slaked lime and very finely ground. Slag cement must not be confounded with Portland cement made from slag. Several new forms of slag cement have recently been introduced. These consist in granulating slag of proper composition with water and mixing the slag so obtained with a small percentage of Portland cement clinker. The "Passow Cement," manufactured in Germany, is of this class.

XIV

CLAY, BRICK AND POTTERY

ALLEN ROGERS

Clays. This is the term applied to such natural-occurring earthy materials having the property of plasticity when wet, which on heating to a high temperature become hard and retain the shape of the molded article. Clay is of secondary origin and, as a rule, results from the weathering of feldspathic rock, such as granite. When found overlying the rock from which it was formed it is termed primary or residual clay. When washed from the original bed and deposited elsewhere it is known as secondary clay.

Plasticity is the property which makes clay valuable in the manufacture of clay products, without which it would be comparatively useless. Many theories have been advanced to account for this physical property, the most generally accepted being the "*Water of Hydration theory*," which is based upon the relation of plasticity to the amount of hydrated silicate of aluminium present. Among other theories which have been advanced may be mentioned the "*Plate theory*," "*Interlocking-grain theory*," "*Ball theory*," and "*Colloid theory*."

Classification of Clays. "Clays may be classified according to their origin, physical and chemical properties, or uses."[1] Of the several classifications that of Orton only will be given and is as follows:

High-grade clays. (50 per cent or more kaolin with silica)	1. Kaolin 2. China-clay 3. Porcelain clay 4. Fire clay (hard) 5. Fire clay (plastic) 6. Potters' clay
Low-grade clays (10 to 70 per cent kaolin with notable per cent of fluxing elements)	1. Argillaceous shale Paving block 2. Ferrugenous shale Pressed brick 3. Siliceous clays Sewer-pipe and paving brick 4. Tile-clays 5. Brick clays 6. Calcareous shale Brick

[1] "Clays, Their Occurrence, Properties and Uses," Heinrich Reis, New York, 1908.

Kaolin. This term applies to the white-burning clays which are composed almost wholly of silica, alumina and chemically combined water, with only a very small percentage of fluxing material such as iron. Their formation is principally due to the weathering of pegmatic veins, although in some cases they have originated from granite, quartz, and limestone. When mined they contain a greater or less amount of the parent rock which is removed by subsequent washing. It occurs quite widely distributed in the United States, east of the Mississippi, while less important deposits are found in Missouri, Utah, and Texas. It is used in the manufacture of white ware, porcelain, tiles, and as a filler for paper.

Ball Clay. These clays are white burning, but differ from the kaolins in that they are plastic in character. They find extensive application in the manufacture of white ware, being used for the puprose of giving the necessary plasticity and bonding power. They must be as free as possible from iron oxides and possess considerable tensile strength. These clays occur mostly in Florida, Kentucky, Tennessee and New Jersey.

Fire Clays. This term applies to such clays as are capable of withstanding high temperature. They owe their refractiveness in most part to the large amount of silica and small amount of fluxing agents which they contain. Fire clays vary widely in their physical and chemical properties, showing great differences in color, plasticity, texture, and tensile strength. They are, as a rule, light in color, ranging from gray to yellowish-red. The deposits may be of either primary or secondary origin. They may be divided into plastic and flint clays, the former being plastic when wet; while the latter are hard and flint like, even when finely ground, but they are very highly refractory. They occur quite widely distributed over the United States. The principal uses of fire clays are for the manufacture of fire-bricks, retorts, furnace linings, crucibles and terra cotta; while a special grade is also used for making pots and tanks for glass manufacture.

Stoneware Clays. These clays differ from fire clays in that they produce a very dense body when heated at a comparatively low temperature. In many instances, however, they are very refractory, but must possess sufficient toughness and plasticity to be worked on the potters' wheel. In making stoneware it is usually customary to employ mixtures of clays so as to produce certain characteristics in the finished product. Stoneware clays are used in the manufacture of stoneware vessels as well as yellow ware, art ware, earthenware and even terra-cotta.

Terra-cotta Clays. The clays used for making terra-cotta differ quite widely, although most manufacturers prefer a semifire-clay. Buff burning clays are commonly used, because of the hard body produced on burning. Those suitable for this purpose are found mostly in New Jersey, Pennsylvania, Indiana and Missouri.

Sewer-pipe Clays. The clays employed for this purpose are quite similar to those used in the manufacture of paving brick. The easily

fluxing clays are of advantage here as the higher iron content aids in the formation of the salt glaze with which the pipes are covered. Some fire-clay is usually employed in the mix in order to retain the shape of the tube during the burning.

Brick Clays. In making common brick, low grade red-burning clays are usually employed. The principal requirement is that the clay shall mold readily and burn hard at a comparatively low temperature. Owing to the market price being low it often happens that poor bricks, which are made from local deposits, are used for structural purposes where a better material should have been employed. Pressed brick, on the other hand, call for a higher grade of clay. The physical requirements here are uniformity of color in burning, freedom from warping, absence from soluble salts, with sufficient hardness and low absorption when burned at a moderate temperature.

Paving-brick Clays. A great variety of materials are employed for this purpose, although those mostly in common use are made from impure shales. These shales are widely distributed. They should have a fair degree of plasticity and a good tensile strength.

Slip Clays. These clays contain a large amount of fluxing material which melts at a low temperature, forming a natural glaze of greenish-brown glass.

Gumbo Clays. Included in this class are certain fine grained, plastic and tough clays, which on account of their shrinkage on burning cannot be used for brick making. Their chief use is in the manufacture of railroad ballast.

Retort Clays. These are dense burning, plastic, semi-refractory clays, employed mostly in the manufacture of gas and zinc retorts.

Pot Clays. The clays coming under this head are hard burning and are employed in the manufacture of pots for glass making.

Ware Clays. These clays are the same as ball clays.

Pipe Clays. These clays are the same as sewer-pipe clays.

Sagger Clays. This is the term applied to those clays which are used in making the saggers in which high-grade pottery is burned.

Portland-cement Clays. In the manufacture of Portland cement a mixture of lime and clay is employed, as given in Chapter XIII. They may be either true clays or shales.

Paper Clays. In order to give body, weight and finish to certain papers, some form of clay is usually employed. The clay, which should be of a plastic nature and of light color, is mixed with the pulp in the beater engine where it becomes enmeshed.

Paint Clays. Many of the clays mix well with linseed oil and form a good grade of paint. The color of these clays varies from light yellow to a dark reddish brown, due to the presence of iron oxide and in some instances to that of manganese. The chief clays coming under this heading are the ochers and siennas.

Uses of Clay. In order to show the varied and numerous applications of clays the table compiled by R. T. Hill and amplified by Heinrich Reis will be given:

"*Domestic.* Porcelain, white ware, stoneware, yellow ware, Rockingham ware for table service and for cooking; majolica stoves; polishing brick; bath brick, fire-kindlers."

"*Structural.* Brick; common, front, pressed, ornamental, hollow, glazed, adobe; terra-cotta; roofing-tile; glazed and encaustic tile; drain tile; paving brick; chimney-flues; chimney-pots; door-knobs; fireproofing; terra-cotta lumber; copings; fence-posts."

"*Refractories.* Crucibles and other assaying apparatus; gas-retorts; fire-bricks; glass pots and blocks for tank furnaces; saggers; stove and furnace bricks; blocks for fire boxes; tuyers; cupula bricks; mold linings for steel castings."

"*Engineering.* Puddle; Portland cement; railroad ballast; water conduits; turbine wheels; electrical conduits; road metal."

"*Hygienic.* Urinals, closet bowls, sinks, washtubs, bathtubs, pitchers, sewer-pipe, ventilating-flues, foundation-blocks, vitrified bricks."

"*Decorative.* Ornamental pottery, terra-cotta, majolica, garden-stands, tombstones."

"*Minor uses.* Food adulterant; paint fillers; paper filling; electric insulators; pumps; fulling cloth; scouring soap; packing for horses' feet; chemical apparatus; condensing worms; ink-bottles; ultramarine manufacture; emery wheels; playing marbles; battery-cups; pins; stilts and spurs for potters' use; shuttle-eyes and thread-guides; smoking-pipes; umbrella-stands; pedestals; filter-tubes; caster-wheels; pump-wheels; electrical porcelain; foot-rules; plaster; alum."

Building Bricks. There are many forms of building bricks including common building bricks, pressed bricks, glazed bricks and enamel bricks, but as space does not permit a complete description of each only the manufacture of common building brick will be given. The processes involved may be divided into the preparation of the clays, the molding, the drying and the burning.

Preparation. Since only a few clays can be used directly as mined it becomes necessary to subject the material to weathering agencies. This is done by spreading the clay over the ground in a thin layer of from 2 to 3 ft. in depth, and allowing it to remain thus exposed for a considerable period, lasting in some cases a year or more. In order to hasten the process, however, some clays are disintegrated by artificial means, for which purpose crushers, edge runners, disintegrators and roller mills are employed. The grinding is usually done on the dry clay, although in some cases the wet clay is used and the process is known as tempering.

Ring Pits. These are pits about 25 ft. in diameter and from 2 to 3 ft. deep. A heavy iron wheel is arranged by means of gears so that it travels in the pit and causes a thorough mixing of the mass. The opera-

tion lasts from 5 to 6 hours at the end of which time the clay is ready for the brick machine.

Pug Mills. These machines are of different shapes and capacity, but are all provided with blades which cut up the clay, produce a thorough mixture and pass it along to the discharge end. They do not take up as much room as the ring pit and are much more readily handled.

Molding. The simplest form of molding consists in pressing the soft clay or mixture into wooden frames which have been dusted with sand to prevent sticking. This operation is done either by hand or by machine and is known as the *soft-mud process.* In the so-called *stiff-mud process* the clay is tempered with much less water. The prepared clay is forced through a die in the form of a rectangular bar, which is then cut into lengths of the brick. The machine employed for this purpose is provided with an auger screw and runs in a cylinder which tapers at the end to the size of the die. Dry pressing is sometimes done as well as semi-dry pressing. In either case the prepared clay is forced with great pressure into steel molds.

Drying. After molding, the bricks must be dried before burning. This may be accomplished in several ways, the simplest being to spread the bricks over a smooth flat floor and allowing them to dry in the sun. Pallet driers are covered frames on which the bricks are placed as they come from the machine. Drying in the air has the disadvantage in that it cannot be used in cold or damp weather. To overcome this many brickmakers are employing drying tunnels. In this method the green bricks are placed on cars and run in at the cooler end of the tunnel and gradually pushed along to the warmer end. These tunnels are built in a variety of ways, but when possible the waste heat from other operations is employed.

Burning. The bricks having been thoroughly dried are placed in kilns and heated to a comparatively high temperature or "burned." The temperature and time of heating depends upon the kind of clay employed and the degree of hardness desired. The kilns may be either "up-draft" or "down-draft." In the former system the heat from the fire passes into the body of the kiln and up through the ware, finally escaping at the top. The heat in the down-draft kiln enters at the top, passes down over the ware and escapes through flues at the bottom.

Continuous or ring kilns are also employed. They consist of a series of chambers arranged in the form of a circle, connected with each other and with the stack by means of a series of flues. The fire is built under the chamber which is to receive the highest temperature; from here the heated gases pass to the next chamber and so on to the freshest charge. In order to utilize the heat from the cooling bricks, after they have reached their maximum temperature, the air supply to the fire is drawn through the chambers containing the thoroughly burned and cooling bricks.

Sewer-pipe Manufacture. Most sewer-pipes are made from shale, which after crushing is mixed with the necessary amount of plastic material

and made into the desired shape by a special form of press. The drying and burning is then carried out in a somewhat similar manner as that given for brick.

Hollow Structural Material. Included in this classification are fireproofing terra-cotta lumber, hollow blocks and hollow bricks. The fireproofing materials are those which are employed in floor arches, partitions, and wall furring for girders and columns. Terra-cotta lumber is a soft and porous material produced by mixing sawdust with the clay and subsequently burning it out. This being soft can be nailed the same as lumber. Hollow block and hollow brick are used for outside walls.

Fire Bricks. Most of the fire bricks on the market are made from a mixture of several clays to which has been added a certain amount of ground fire brick or quartz. They are made in many shapes and vary greatly in hardness and their degree of refractory power. The burning is almost universally conducted in down-draft kilns.

Tile. Under this heading comes roofing tile, floor tile and wall tile. They are made in a variety of ways and from a variety of materials. Some are made in a porous condition while others are colored and highly glazed.

Pottery. This heading includes a great variety of products ranging from the cheap earthenware, such as flower-pots, to the most delicate porcelain vase. In the manufacture of pottery there are certain operations which are common to all, but with the higher grades much more care and a larger number of details are necessarily involved. The general operation consists in the preparation of the raw material, tempering, molding, drying, biscuit burning, dipping, glost-burning and decorating.

Stoneware. This class of material is made from low-grade plastic clay, being porous in character, red to cream in color and may or may not be glazed. If the object is to receive a glaze, it is usually developed with the body so that after drying the object is in a proper condition for the application of the glaze. Slip-clay, which is largely used for this purpose, melts to a brown glass at the temperature at which the ware is burned. Salt glazing is a very simple method and is in common use for this kind of ware, although it is applied more especially to sewer-pipe. The goods having been placed in the kiln and the maximum temperature reached, the salt is thrown into the fire. The high temperature causes a volatilization of the salt which on coming in contact with the clay unites with it, forming a glaze on the surface of the ware. In yellow ware the object is burned to develop the body, after which the glaze is applied and the ware heated a second time.

White Ware. Included in this class are those products having a white or nearly white body and usually glazed. Mixtures consisting of kaolin, ball-clay, quartz, and feldspar are the materials which are employed and these are selected with the idea of their white-burning qualities in view.

Porcelain. Prior to the sixteenth century, this term was used to designate those objects made from mother-of-pearl. At the present time, how-

ever, the same materials are employed for making porcelain as those used for white ware. Great care, however, must be exercised in their selection and the mixtures so proportioned as to give a hard and translucent body. That in which spar is used for the flux is known as hard porcelain and is bluish white by transmitted light, while that fluxed in part with calcium phosphate, known as bone china, is yellow by transmitted light.

Glazes. For all pottery, except hard porcelain, the ware is first burned in the biscuit kiln, forming porous porcelain, then glazed and burned again in the glost-kiln. The glazes consist of mixtures of acids and bases so combined that they will melt to a glass at the temperature of burning. It is very important also that the coefficient of expansion agrees with the body of the ware, otherwise a defective glaze will be the result.

XV

GLASS

JAMES GILLINDER

Gillinder Sons, Inc., Glass Manufacturers, Philadelphia, Pa.

GLASS is an amorphous product of fusion, differing widely in composition. Ordinarily it is considered as a mixture of an alkaline silicate and the silicate of one or more bases, the alkali being sodium or potassium, the base calcium or lead, while sometimes all four elements enter into its composition. While this is true of nearly all commercial glass, it must be noted that at Jena and elsewhere glasses have been made free from alkali, that borates and phosphates have been substituted for silicates, and that many elements such as zinc, barium, magnesium and antimony have been substituted for lead and lime so that it is practically impossible accurately to define glass.

Technically, transparent glasses are divided into lime glass or lead glass according to the presence of these elements. The term flint glass, which originally meant a pure lead potash glass, is now often applied to all clear transparent glass. Sometimes the lime glass is called lime flint or German flint. Bottle and window glass are impure forms of lime glass. White or "opal" glass and colored glass are glasses to which materials have been added to produce the color effect.

The following are the chief raw materials used in making glass:

Silica. Silica is usually introduced in the form of sand, which may vary in purity, according to the source and care in preparation. The chief impurities in sand are iron, alumina and organic matter. The presence of a small amount of alumina does not injure the glass, but iron acts as a coloring agent, producing a green of more or less intensity, depending on the quantity present and the state of oxidation. For the finer glass, therefore, a sand as free from iron as possible is required, while for more common ware, such as green bottles, a much larger quantity is permissible. Sand from Berkshire, Mass., is practically free from iron, while that from Pennsylvania and West Virginia often contains less than one-tenth of one per cent. Sand from New Jersey usually has a much higher iron content.

The sand must be of uniform size, not too coarse, to prevent reaction with the other material, nor yet so fine as to cause the reaction to take place too violently and cause excessive foaming during the melting.

Natural silicates, such as feldspar, are sometimes used as a source of silica, because of the alumina and alkali which they contain. Slags from metallurgical processes have been used for common ware with varying success.

Alkali Metals. *Sodium carbonate* (soda ash), produced either by the Solvay or the Leblanc processes, is the chief source of soda and is obtained from the trade in a pure condition. *Sodium sulphate* (salt cake), owing to its cheapness, is also used in the manufacture of plate and window glass. Its use requires the addition of carbon as a reducing agent and is attended with many difficulties not met with when the carbonate is used. The amount of carbon added is much less than that called for by theory and it is impossible to give an exact explanation of the reaction. *Sodium nitrate* (Chile saltpeter), either as it comes from Chile (95 per cent) or refined for the better ware, is used as an oxidizing material to destroy organic matter and to change the iron to the ferric condition. *Potassium carbonate* (pearl ash, potash, salts of tartar) usually hydrated, containing from 80 to 85 per cent potassium carbonate, is the chief source of potassium in the glass industry, sulphates and chlorides being the chief impurities. In some European factories crude pearl ash from the sugar refineries is used in the cheaper kinds of glass. *Potassium nitrate* is also used as an oxidizing material.

Alkali Earths. *Calcium* is introduced as a carbonate, oxide or hydrated oxide. Limestone occurs in nature of sufficient purity for use after simply grinding. Burnt lime is also used, but more frequently the hydrated oxide. The advantage of the different forms of lime is an open question, some works preferring one, some another. The advantage of burnt lime is the saving in heat by the removal of the carbon dioxide before entering the furnace, while on the other hand the liberation of carbon dioxide from the carbonate helps stir the glass during the melting process. Iron in all glass-making materials is harmful, while magnesia makes the glass hard and more difficult to "plain," though many American factories use a lime high in magnesia content without any apparent disadvantage. *Barium* is sometimes used in the form of sulphate together with carbon, but more generally as a carbonate either natural or prepared. It produces a glass high in refractive power and is used for many optical purposes.

Heavy Metals and Acid Radicals. *Lead* is used generally as red oxide or litharge to impart brilliancy and to produce glass of high refractive power. Red lead, because of the oxygen which it liberates, is preferred to litharge. Freedom from metallic lead and discoloring metallic impurities, such as copper and iron, is required. *Zinc* is used as oxide to replace lime or lead, especially in the modern heat-resisting glasses. It is also largely used in opal glass. *Boric acid* and *borax* are used in optical and heat-resisting glass as well as in colored glasses. *Phosphate of lime*, bone ash, is used to produce opalescence or opacity depending upon the quantity.

Bone ash, unless it is present in large quantity, requires "reheating" to bring out the opalescence. *Feldspar* is used as a source of alkalies and alumina. Used with fluorspar it produces opal glass. *Fluorspar* used with feldspar or alumina produces opal glass. Iron and metallic sulphides (lead and zinc) are the chief harmful impurities. *Cryolite. sodium aluminium fluoride*, used alone, produces dense opaque glass, but owing to its solvent action on the clay pots other materials are taking its place. It is largely used in making opal glass by the tank method. *Arsenic* as white oxide is used in opalescent and opal glass and in enamels. *Tin oxide* is used to a limited extent in colored glasses and in enamels. *Antimony* as oxide, sulphide or metal is used in colored glasses and the sulphide is employed in tank glass to "improve the color."

Coloring Materials. *Uranium*, usually as sodium uranate, is used to produce a peculiar yellow fluorescent glass. When in the ferrous state, *iron* colors glass green, and yellow when in the ferric condition. The temperature of the furnace, however, materially affects the state of oxidation of the iron, a high temperature changing it from yellow to green (see manganese.) As a colorant it is usually added as red oxide or iron scales. *Chromium* produces green and greenish-yellow glass. The oxide Cr_2O_3 is very hard to dissolve; hence potassium dichromate or other metallic chromates are used. *Manganese.* Black oxide, MnO_2, is the most used of all the coloring oxides. In large quantities it produces black, and in less amount purple to light pink color. It is used to correct the color effect of iron, which is always more or less present in glass material. It acts as an oxidizing agent also. The quantity of manganese to be used depends on the amount of iron present and the temperature of the furnace, as the hotter the furnace the more manganese is required. The heat "burns out the color." (See under Iron.) The impurities met with are iron and earthy matter, while cobalt is sometimes present in sufficient quantities to be harmful. *Nickel*, as oxide, is used in a very limited way. European practice substitutes it for manganese in some glasses, but American factories have not found this satisfactory. *Cobalt*, as oxide or smalt, is employed in giving an intense blue color. The blue from cobalt shows purple by transmitted light. *Gold* as chloride or purple of Cassius, is used to produce a ruby color. *Copper* in the cuprous form produces red, in the cupric it produces a peacock-blue color. *Selenium* is used to produce a red color. *Cadmium sulphide* forms a lemon yellow color in lead-free glass. Both cadmium and selenium are usually added after the glass has been melted in the pot. *Carbon* is used as a reducing agent in sulphate glass. In the form of coke, oats, bark, and other organic matter it produces an amber color in lime glass.

Pot Furnaces. Furnaces in which the glass is melted in clay crucibles or pots are known as pot furnaces, while those in which the glass is melted in one large rectangular clay tank are known as tank furnaces or tanks. Pot furnaces are either open or closed, and may be fired either direct,

regenerative or recuperative. Tanks are either "day" or continuous, working either intermittently or continuously. The direct fired coal furnace is still used, but the regenerative furnace is the most satisfactory and economical of pot furnaces, illustrated in Chap. V. In this type the burnt gases from the furnace are made to pass through fire brick checker-work flues which then become highly heated. The direction of the draft is then reversed by suitable dampers, and the incoming air and gas are led through; while the burnt furnace gases go to heat another checker work which has become cooled by the incoming air and gas of the previous run. Thus the burnt furnace gases give up their waste heat to the checker work, which in turn gives it up to the incoming gas and air. In practice this reversal of draft is made every twenty or thirty minutes. In the recuperative furnace there is no reversal of draft, but the hot burnt gases pass through clay tubes which by conduction give up their heat to the incoming air and gas. This furnace is used abroad, but has not been adopted widely in America.

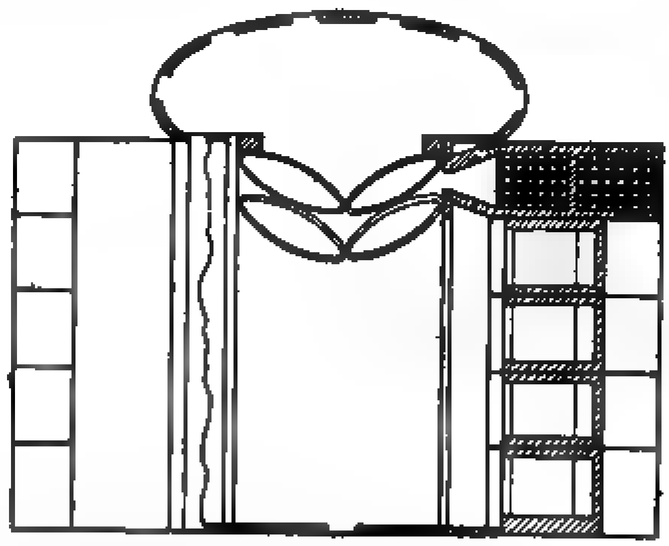
Tank Furnace. The introduction of the tank furnace marked an epoch in the glass industry. The batch is put in a shallow fireclay tank covered with a refractory arch of silica brick and heat applied to the surface of the batch. The simplest form is the intermittent or "Day Tank." The batch is shoveled in, the work holes are closed and heat is applied, either oil or gas being used. When the glass is "plain" the heat is reduced, the work holes opened, and when cooled sufficiently the glass is worked. These tanks are filled in the afternoon and are ready to work the following morning, hence the name. To obviate the loss of heat by this method continuous tanks are used. These are usually much larger than the day tanks and are usually divided into compartments by fireclay obstructions. The batch is filled in at one end of the tank, Figs. 176, 177 and 178, and after melting flows under the obstruction to the working end. As fast as the glass is worked out, a new batch is introduced so that the melting and working go on continuously, thus maintaining a nearly constant level of glass. The continuous tank is the most economical form of glass furnace, and wherever large quantities of glass are made, it is used. The glass produced is not so good in color as that made in closed pots, so that for the finest ware or where small quantities are made, pot furnaces are still employed.

The air and gas passing through the hot checker-work A, B, burn, pass through the melting compartment and out to the slack, giving up their residual heat to the checker-work A_2, B_2. In about twenty minutes, when A and B have become cool and A_2 B_2 hot, the direction of the draft is reversed. By such reversals a minimum of heat is lost and a maximum temperature maintained.

The temperature of the glass furnace is indicated by means of pyrometers chiefly of the thermo-electric type. A temperature of 1400–1500° C. is usually maintained in pot furnaces, while in tanks the tem-

perature runs somewhat higher. It is not safe to run much above this, owing to the danger of melting the pots and the furnace materials.

Melting Pots. These are of two kinds –open and covered. The covered pots are used in making flint glass, the open ones, which are rapidly being replaced by tank furnaces, are used for green and plate glass. The manufacture and handling of glass pots require great care. The fireclay is carefully mixed with ground burnt clay (old potshell), and after moistening is worked into a doughy mass. Men then tramp this mixture with bare feet to increase its plasticity, and after several months of aging it is ready for use. The bottom of the pot is first formed by making a layer of clay four or five inches thick, then the sides are built up a few inches at a time, the clay being worked by hand into the already built-up part, Fig. 180. When not being built they are covered with damp cloths to keep the clay moist. After the pot is finished it is allowed to dry in a warm room of constant temperature, and away from drafts. After several months the pot is ready for use; but before it can be placed in the stack it must be gradually raised to the temperature of the furnace. This preliminary heating is done in an auxiliary furnace known as a pot arch, Fig. 181. Having been raised to a white heat the pot is transferred to the place in the furnace made vacant by a broken pot. This operation is known as "pot setting." Before using, the pot is glazed with molten glass to retard the action of the batch upon it.



Horizontal section showing where batch is fed in, and clay obstructions known as floaters under which the glass must flow to reach the working end.

FIG. 176.—Continuous Tank.

F = flues for gas and air;
A, A_1 = air checker work;
B, B_1 = gas checker work;
P = ports for entrance and exit of gas and air;
C = silica brick arch.

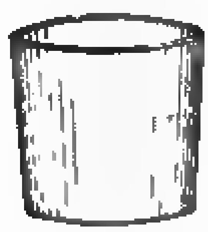


FIG. 177.—Open Pot.

Pots vary in size from those holding but a few pounds (known as monkeys) to those holding several tons. The life of a pot varies greatly.

It may be broken from the outside by a sudden change of temperature, or by one of many other causes, but the natural end of a pot is by corrosion from the inside. This corrosion varies with the different kind of batches. Some pots may last but a few weeks, while others may remain perfectly good for a year. Sometimes a pot is taken out before it breaks because it is introducing small pieces of clay (stones) into the glass.

Melting Process. The batch, made by weighing and carefully mixing the various materials together with some broken glass (cullet), is filled into the pot and the stoppers luted on. After this charge has melted more material is added until the pot is full; usually one such "topping" is sufficient to do this, but sometimes it must be repeated. Some factories do not top excepting over Sunday, but get the glass quicker during the week with "one filling." Test pieces (proofs) are taken out from time to time on the end of an iron hook. The glass at first shows

FIG. 178.*—A Type of Continuous Tank, showing another form of obstruction—a wall with an opening at the bottom through which the glass flows to the working end.

opaqueness, gradually becoming vitreous and transparent, but full of small bubbles (seed). As the melting proceeds, however, these bubbles become fewer and larger and finally when they have all "gone off" the pot is "plain" and ready to "take down." The stoppers are now removed and the pot allowed to cool, either naturally or by blowing air into it. The dirt and impurities are removed from the surface and the glass or "metal," as it is called, is ready to work. The ordinary practice is to work a covered pot every other day, but where the pots are not topped or the furnace is very hot they may be worked oftener. No definite time, however, can be given for the length of melting, as it varies with the size and thickness of the pot, the kind of glass being melted and the temperature of the furnace.

The reactions taking place in a glass furnace cannot be given with any degree of accuracy, but the process of the fusion is the union of the bases and silica to form mixed silicates with the liberation of carbon dioxide and in some cases oxygen, sulphur dioxide or other gases.

FIG. 179.*—Exterior of Continuous Tank, showing side ports and filling end.

Among the defects of glass are the following:

Seedy. Containing small bubbles of unexpelled gas. This is caused usually by too low a temperature or not sufficient time in melting. Some glasses (especially optical glass containing barium) are impossible to plain.

Fig. 180.*—Making Pots, showing how the clay is worked in by hand and monkey pots in various stages of manufacture.

Stony. Containing undissolved portions of batch or small particles of clay from the walls of the pot or tank.

Cordy, wavy. The glass not being perfectly clear, but having threads or more or less sharpness running through it.

High Color. Pink from excess of manganese.

Low Color. Green from excess of iron.

Processes of Manufacture. The working of glass depends upon the fact that it passes from a liquid to a solid state without crystallization and possesses, when in a hot condition, ductility and malleability to an extreme degree. The physical properties of glass are well known.

Fig. 181.—Covered Pot, showing pot arch. This pot weighs about 3000 lbs. and will hold two ton of batch.

Casting. Plate glass is made in open pots that can be removed from the furnace and their contents poured on a casting table and then rolled to the desired thickness by a metal roller. (Fig. 182.) The plate of cast glass is then transferred to a kiln or annealing oven (lehr) and gradually allowed to cool. After the plate, which is rough and uneven, is cooled, it is fastened to a table with plaster of Paris, ground with revolving iron rubbers and sand, first coarse, then finer until the surface is even and smooth. It is then polished by felt-covered rubbers and rouge paste. The plate is then reversed and the other side ground and polished.

Fig. 182.*—Removing a Pot of Plate Glass from the Melting Furnace to the Casting Table.

Unpolished plate glass, known as rough plate, is made similar to regular plate glass excepting that the glass is taken from the pot in large steel ladles and poured on a table between guides. The table or the roller often have a design on them, thus producing ornamental effects in the glass.

Fig. 183.*—Casting Plate Glass.

Wire glass is rolled plate in which wire has been imbedded during the rolling process. Special care is necessary to prevent this glass from flying apart owing to unequal expansion of the

* Cuts loaned by H. L. Dixon Co., Pittsburgh.

glass and wire. Polished plate glass of opal and black glass have been made and used for table tops, sanitary wall, and for other purposes.

Pressing. Glass is gathered on the end of an iron rod (punty) by revolving it rapidly in the molten glass. It is then carried to the workman (presser), who cuts off with shears the amount desired and allows it to drop into the mould. A metal plunger is then forced into the mould and forces the glass to fill the space between the plunger and the mould. Fig. 185. When the glass has become firm, the plunger is withdrawn, the mould opened and the article either sent direct to the annealing oven or first reheated in an auxiliary furnace (glory hole) to remove mould marks or to alter the shape.

FIG. 184 *—Starting a Cylinder of Window Glass.

FIG. 185.*—Moulds for Pressing and Blowing a Bottle.
M = press mould; *R* = ring; *P* = plunger; *N* = blow mould; *G* = glass.

Press moulds are made of cast iron and so constructed that the pressed article can be easily removed. The temperature of the mould and plunger is regulated by streams of air blown against them, the expansion and contraction of the mould being carefully controlled by the workman. The plunger is usually operated by hand power, but for some purposes steam or compressed air is used.

Blowing. Window glass until recently was entirely hand made, but machines are being introduced which are replacing hand labor. In the hand-made glass the workman gathers a lump of glass on the end of a hollow iron pipe and after cooling it a little, introduces it into the molten

glass and gathers more. This is repeated until he has sufficient for his purpose. Then by blowing and swinging and further manipulation (Fig. 186), he produces a large cylinder of glass. The surplus glass is cracked off the ends of the cylinder and it is cracked lengthwise for the next operation. Fig. 187. The cylinder is then gradually heated in a flattening oven and as it begins to soften it is flattened by rubbing on a flat stone, after which it is transferred to the annealing oven and gradually withdrawn from the heat.

Fig. 186.*—Blowing Window Glass.

Window glass is now generally made in continuous tanks, which have replaced the old open-pot furnaces.

Machine-made window glass is made by immersing a blowpipe in molten glass, introducing compressed air and gradually withdrawing the blowpipe from the molten glass. By carefully regulating the speed of withdrawal and the amount of air introduced cylinders of any length are made and flattened as usual.

Another process which has not passed the experimental stage is to replace the blowpipe by a flat bar and passing over rollers into a continuous lehr produce a continuous sheet which is cut off and selected as it comes from the lehr.

Fig. 187.*—Splitting a Cylinder of Window Glass Preparatory to Flattening.

Crown Glass. Crown glass, once the chief source of sheet glass, is now made only for special purposes, such as microscope slides and cover glasses, where a surface free from imperfections is required. It is made by blowing a ball of glass, attaching to the side away from the gathering iron a hot iron rod (punty) and cracking it off the gathering iron. The glass is then heated and rapidly revolved until it forms a large flat disk, when it is annealed and selected.

Hollow Ware. Hollow ware is shaped in moulds of metal or wood. The glass is gathered on a hollow pipe, and after shaping by rolling on a polished plate (marver) or revolving in a hollow iron or wooden block it is blown into the mould and takes its shape. Fig. 188.

FIG. 188.*—Blowing Lantern Globes.

In the case of chimneys, tumblers and other cylindrical articles the glass is revolved in the mould and shows no joint or mould mark. Such moulds are lined with charcoal or special paste which enables the glass to be turned. In the case of lantern globes or articles with raised or sunken patterns the glass is blown without turning and takes the exact impression of the mould (iron mould).

Bottles. Bottles are made by blowing in a mould, and after reheating the neck is finished with a special tool.

The recent advances that have been made in the making of bottles and fruit jars, combine pressing and blowing. A blank is pressed in a mould having the shape of the neck and with a weight of glass sufficient to make the bottle. This blank is then removed by means of a ring and placed in a mould the shape of the finished bottle and blown to shape by compressed air. Fig. 189. In some machines a gatherer and presser are required, in others only a gatherer, while in the Owens machine the entire operation is done mechanically. In this machine the glass flows from a melting tank into one which, revolving, carries the molten glass to the machine. The machine sucks up sufficient glass to make the bottle and at the same time forms the neck. It is then carried to a mould in which it is blown to its final shape. Machine-made bottles are rapidly displacing the hand-made ones.

Large objects, such as vats, jars and even bathtubs have been made by the Sievert process. Molten glass is cast on a perforated metal table and after being properly distributed the chilled edges of the glass are clamped and the table turned over. The hot glass sags and is then blown into shape by compressed air. A mould or other form is used to give the desired shape.

Optical Glass. Optical glass is usually made in a one pot furnace and differs from other glass in being allowed to remain in the pot until

FIG. 189.*—Pressing and Blowing Machine. On the left the press; on the right the device for blowing with compressed air. See Fig. 188.

it has become cool. The batch is melted and after it has become "plain" is stirred with a burnt fire-clay rod to produce uniformity and destroy striæ. Then the glass is quickly cooled until it loses its fluidity, and after this it is very gradually cooled. When cool the pot is broken open and the glass sorted. Only a small portion is fit for use. In recent times advances have been made in this kind of glass, especially at Jena, where many of the optical glasses have originated.

Annealing. In all the processes of manufacture, with but few exceptions, the finished articles while still hot are taken to an oven and gradually cooled. If glass is cooled suddenly it develops great internal strain so that it is likely to fall to pieces under change of temperature or when its surface is scratched. An extreme case of sudden cooling is the Prince Rupert drop, a piece of glass produced by dropping a bit of molten glass

tough, but if scratched with a file or its thin tail broken the drop flies into a fine powder. Glass possessing internal strain is readily detected under polarized light.

To obtain glass free from strain it must be "annealed" or cooled gradually. This is accomplished either by placing the finished article in a heated room and allowing the fire gradually to die out (kilns or ovens) or by gradually withdrawing the article from the heat (leers). The former method is used for heavy articles such as carboys, plate glass, blanks for cutting, and optical glass, while the continuout lehr is used for lighter ware. Recently, however, such improvements have been made in continuous leers that large articles and even plate glass can be successfully annealed in them.

The time of annealing varies from a few hours in the leers to a week or more in the kilns, depending on the thickness and composition of the glass. In annealing optical glass the cooling is carefully controlled and of long duration, as any sign of internal strain renders it unfit for use.

Colored Glass. *Amber* is produced by the addition of carbonaceous matter, e.g., grain, coke, coal, sawdust, or other organic matter, to a lime glass. The intensity and shade of color depend on the kind and quantity of matter added. Amber is also produced by sulphur and certain sulphides. *Black* is produced by an excess of coloring matter such as manganese, cobalt, or iron. *Blue* can be produced by cobalt or copper. When produced by cobalt it is dark, showing purple by transmitted light. The copper blue is a less intense color, bordering, on the green. *Canary*, a special color produced by uranium. See yellow. *Green.* Chromium or iron alone will produce a green glass, though it is usually made by combining several oxides, such as copper and iron or chromium and copper. *Gray*: "London Smoke." When substances producing complementary colors are added to the same glass a gray color is produced. *Opalescent.* Glass resembling the opal is produced by the addition of arsenious oxide and calcium phosphate. When this glass comes from the pot it is colorless, but on allowing it to cool and then reheating, the opalescence is developed. If the cooling is carried too far the opalescence is lost and a milky effect produced. Opal or white opaque glass was originally produced by the addition of cryolite or an excess of calcium phosphate into cold water. Instead of flying to pieces it becomes very hard and (bone ash). Mixtures of fluorspar and minerals containing aluminium, such as feldspar, have been substituted and recently artificial compounds bearing fluorine, such as aluminium fluoride, and sodium silico fluoride, have been used. *Purple* is produced by manganese dioxide. *Red* or *Ruby* is produced by gold, selenium or copper. In the use of copper great care is required to have the copper in the right condition of division and reduction. The glass, as it comes from the pot, is usually light green in color but on cooling and reheating an intense red (such as is used for

railroad signal lights is produced. The color, however, is usually too intense for use alone so it is " flashed " by gathering a small quantity of the ruby glass and then covering it with sufficient clear glass to make the desired color. " Flashing " is frequently resorted to in making colored sheet glass. Gold ruby is worked very much the same as copper ruby, excepting it can be produced sufficiently light in color to be used alone, though flashing is often used to reduce the intensity. Gold ruby as it comes from the pot is colorless or yellow, but when properly cooled and reheated develops the ruby color.

The cause of the peculiar action of these and some other glasses has recently been discovered by the researches of Siedentoff and Szigmondi on ultra microscopic particles. They have shown that the metallic gold or cuprous oxide exists in an extremely fine state of division probably held in a mechanical suspension resembling a colloidal solution. Thus it is that if the gold or copper remain in solution, as when they come from the pot, the red color is not produced, but if the correct manipulation of the glass takes place the colloidal solution is produced and the red coloration results.

Artificial gems are highly refractive glasses of purest materials and colored with metallic oxides to imitate precious stones. The colorless glass is known as strass. These glasses are usually soft, because of the arge quantity of lead used to produce the high refractivity.

Finishing Processes. Decorated or painted glass is produced by painting on the glass with easily fusible glazes. These glazes are finely ground, mixed with oil and applied to the object and after drying it is put in a kiln and heated sufficiently to fuse the glazes. Cut glass is usually a highly refractive lead glass which when cut shows a beautiful play of prismatic color. The design is first marked out with red paint and then " roughed " with sand on an iron wheel. It is then " smoothed " on a fine-grained stone wheel and finally polished on a wood wheel with putty and pumice. Of recent years this last operation has been replaced by dipping in strong hydrofluoric acid. Glass is obscured or roughed by means of sand blast or by dipping in a bath of alkaline fluorides.

In etching designs on glass a print is made on paper, using a protective wax as ink. This print is transferred by rubbing it upon the glass. The paper is removed, leaving the ink design on the glass. The inside of the article is now protected by wax and then immersed in hydrofluoric acid. The acid etches the part exposed, but does not affect the parts protected by the ink or wax. The wax is then removed by hot water, leaving the finished design. Often the glass is first obscured by the sand blast and the design etched in the roughened surface.

APPROXIMATE COMPOSITIONS OF VARIOUS KINDS OF GLASS

	Plate.	Window.	Lime Flint.	Lead Flint.
SiO_2	71	71	74	54
PbO	......	......	......	35
CaO	13	11	7	
Na_2O	14	15	19	
K_2O	......	......	......	11
Al_2O_3 } Fe_2O_3	1–2	1–2		

The iron and alumina vary with the purity of the materials.

APPROXIMATE BATCHES FOR GLASS.

Plate Glass.		*Lime Glass.*		*Lead Glass.*	
Sand	100	Sand	100	Sand	100
Soda ash	30	Soda ash	35	Potassium carbonate	35
Limestone	30	Lime	12	Red lead	60
		Nitre	10	Nitre	10

Cullet is added to the above batches in varying proportions.

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XVI

DUTCH PROCESS WHITE LEAD

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Lead. Lead is usually found as an ore in combination with sulphur as lead sulphide or galena. Galena is usually associated with other minerals, from which it must be separated. This is done by crushing, grinding, and concentration until rich "concentrates" are obtained.

FIG. 190.—Casting Lead "Buckles."

The "concentrates" are roasted and smelted. By this treatment the sulphur is driven off and crude lead obtained. This crude lead is then refined to remove the copper, silver, and other impurities, and "corroding pig lead" is obtained.

Corroding. To change this pig lead into white lead, it is subjected to the corroding gases produced by the fermentation of refuse tan bark. Special buildings are provided for this purpose, known as "corroding houses." These "corroding houses" are buildings about 30 ft. high with

floor-space frequently about 20 ft.×40 ft. The floor of this building may be of ordinary earth, and upon it a layer of spent tan bark is placed about 20 ins. thick. On this is placed a layer of corroding pots covering the entire floor, except around the edges where tan bark, known as " banking," is packed.

In each corroding pot about half a pint of weak acetic acid, containing about 2½ per cent of glacial acetic acid, is placed. These pots are then filled with lead buckles. On top of the pots a layer of boards is placed, and on these boards another layer of tan bark. Another layer of pots is placed on this second layer of tan bark; these pots are filled, as with

Fig. 191.—Setting Lead "Buckles" in Pots.

the first layer, and other layers are placed on this until there are from 8 to 10 layers or " tiers " in the stack.

For the corrosion of lead to white lead, a certain amount of ventilation is necessary so that the moisture can be carried off from the stack. This is done in various ways. A typical way is to provide a wooden pipe that shall run from each tier up near the center of the stack to the top. On the top of this pipe is an outlet which may be opened or closed as may be desired.

Chemical Change. When the stack has been built, the tan bark commences to ferment, liberating carbon dioxide, and generating considerable heat. The heat causes the acetic acid to evaporate and its fumes attack the lead buckles. In a short time these buckles are covered with a layer of basic acetate of lead. The carbon dioxide generated by the fermentation of the tan bark then decomposes the basic acetate of lead, producing white lead or basic carbonate and liberating neutral acetate of lead which has a strong

solvent action upon lead itself. This fermentation and corrosion of the lead continues until most of the lead is changed into white lead. At times, the heat generated by the fermentation of the tan bark rises rather high, sometimes exceeding 180° F.

Grinding. When the fermentation of the tan bark has practically ceased and the corroding action is nearly finished, the " stack," as the whole body of tiers is called, is taken down, or " stripped," commencing at the top. The corroding operation takes from 100 to 130 days. When the stack is stripped, it is found that the metallic lead that was originally in the pots has been changed to a white, porcelain-like material, which is white lead. All of the metallic lead originally present has not been corroded however. It is necessary, therefore, to remove the remaining metallic

FIG. 192.—Starting to Strip Stack.

lead, and to grind finely the white lead in order to make it a suitable paint material. This work is done largely in iron machinery that is air-tight, so that the dust formed will not escape. The corroded lead from the stacks is first passed through a screen, covered with sheet-steel perforated with rather large holes. This screen tumbles the lead about, breaking up the white lead sufficiently, so that it passes through the holes in the steel covering, while the large pieces of metallic lead pass out as tailings, to be re-melted for further use. This coarse white lead is then passed through rolls and fine screens to remove the finer metallic lead; following which, the white lead reaches the condition known as " unground carbonate " and becomes suitable for water-grinding. The unground carbonate is mixed with water and ground with high-speed millstones so that every particle will pass through fine silk bolting cloth. The white lead in water after grinding is also floated a long distance so that any coarse and unground particles may settle out. The water

containing the white lead is pumped into large tanks and allowed to settle.

Pulp Lead. The thick mixture of white lead and water, called "pulp," which settles to the bottom, is pumped onto drying pans made of copper and dried with exhaust steam, the product being the dry lead of commerce. This dry white lead is mixed with linseed-oil and ground through burr mills to produce a white lead paste, which is the commercial white lead in oil. Sometimes, the white lead pulp is mixed directly with refined linseed-oil in special mixers, the oil combining mechanically with the white lead, producing white lead in oil of commerce, the water being eliminated. Certain points in connection with the manufacture of white lead by the Dutch process deserve special consideration.

FIG. 193.—Rake Tubs, through which White Lead is Floated.

Corroding Pig Lead. In the Dutch process a very pure pig lead is needed, as the more objectionable impurities are not eliminated to an appreciable extent in the process of manufacture. There are few, if any, metals found in commerce as pure as the best grades of corroding lead.

Impurities. Silver and copper are, however, the most objectionable impurities, and should not exceed 0.0010 per cent. In zinc desilverization by the Parkes process, both silver and copper are removed well below this limit. Bismuth is a common impurity in pig lead; it is not removed by the Parkes process. Refining by the electrolytic process, or by crystallization, as in the Pattinson process, eliminates bismuth. Bismuth is objectionable principally from the manufacturing standpoint, and only occasionally imparts a gray tint to white lead containing it. The manufacturing difficulty occasioned by bismuth is to be found in

its tendency to collect on the millstones in an alloy of lead and bismuth somewhat richer than the original pig lead. Iron does not alloy with lead appreciably, so that in melting pig lead to cast it into buckles, the iron, which may have been present in the pig lead as a mechanical impurity, is eliminated. The maximum solubility of iron in lead is about 0.0015 per cent.

While a very pure pig lead is needed for the manufacture of white lead by the Dutch process, this does not necessarily operate against the process as an element of cost, as the refining of lead is a desilverizing process, and the silver recovered generally pays for the cost of refining. Attempts to manufacture white lead from the low grades of pig lead running relatively high in silver and copper should not, consequently, be favored from the standpoint of economy of operation.

Acetic Acid. The amount of 28 per cent acetic acid used in the corrosion of white lead by the Dutch process seldom exceeds 1 per cent of the lead set. Some of this acetic acid is carried away in the flue gases and is lost, some is eliminated in the wash-water, and the remainder stays with the white lead, combined in some form of insoluble acetate. Ordinarily the amount of acetic acid present is about 0.08 per cent. There is no evidence, based on practical experience, that this acetic acid is objectionable. There is strong evidence that a very much larger percentage of acetic acid may be present without appreciable injury to the product. Very carefully conducted painting tests, show no difference in durability between the ordinary Dutch process white lead and one to which acetate of lead, equivalent to 0.50 per cent of glacial acid had been added.

Fermentation. The micro-organisms, which are in part the cause of the generation of carbon dioxide from the tan bark, have not been isolated, and, so far as I know, attempts that have been made have been unsuccessful in obtaining pure cultures. The indications are that the oxidation of the tan bark in the early stages of the corroding action is due to fermentation produced by micro-organisms, but, when the heat has reached a certain point, the oxidation is in the nature of slow combustion, in which micro-organisms have little or no part.

Pulp-mixed White Lead. We have mentioned how white lead in water can be mixed with linseed-oil, with the result that the oil displaces the water and combines mechanically with the white lead. This is the basis of pulp-mixed white lead. Its manufacture is more sanitary than dry grinding, and this is the principal reason why the pulp-mixed process has been used. Pulp-mixed white lead, however, is somewhat whiter than dry ground, because there is less overheating in the mills, and some of the mechanical impurities, such as tan bark, are eliminated with the water. The amount of water left in pulp-mixed lead seldom exceeds 0.50 per cent, and usually is much less than this. There is no evidence

that this water operates injuriously upon the paint prepared from pulp-mixed lead, nor is there any evidence that pulp-mixed lead is inferior in any respect to the old-fashioned lead ground in chasers and then through burr mills. Evidence, on the other hand, has been obtained that pulp-mixed lead is equal in all its qualities to dry ground, and, in addition to that, it works somewhat better for inside work where what is known as " flat work " is done.

What White Lead is. The name white lead applies to a compound consisting of carbonate of lead and hydrate of lead in chemical union. It is a commercial name, and is distinctive of a definite product which has been upon the market for hundreds of years. During the year 1907, about 130,000 tons of white lead, were manufactured in the United States. This amount, produced in a single year, exceeds the total amount of all straight pigments made from lead or lead ores which annually have ever been produced in the United States. The ordinary formula for white lead is given as $2PbCO_3.Pb(OH)_2$, corresponding to the compositions shown here.

I

	per cent
Lead Carbonate	68.91
Lead hydrate	31.09
	100.00

II

	per cent
Lead	80.12
Equivalent to	per cent
Lead oxide (PbO)	86.31
Carbonic acid (CO_2)	11.38
Water (H_2O)	2.31
	100.00

The evidence that there is a definite compound of this composition is found in the following facts:

First. If carbonic acid gas is passed into a solution of basic acetate of lead, a precipitate is obtained which, at first, may contain a large percentage of basic acetate of lead in more or less insoluble form. As the solution becomes more nearly neutral, however, the composition of the precipitate approaches that given above. The basic acetate of lead which has been precipitated with the white lead is dissolved in the more nearly neutral acetate solution. The indications are that the chemical process in the corrosion of white lead by the Dutch process, involves, at the start, the oxidation of the lead and the formation of basic acetate of lead; that this basic acetate of lead is decomposed by the carbonic acid present, the basic lead being precipitated as white lead; and that the neutral acetate of lead again acting upon more metallic lead is changed into the basic form ready to be acted upon again by carbonic acid. The precipitation of white lead, therefore, from solutions of basic acetate of lead corresponds to the formation of white lead in the stacks after the metallic lead had become oxidized.

Second. Any one who is familiar with the Dutch process of corrosion can, on visiting the corroding stacks, isolate definitely, to his own satisfaction, white lead of theoretical composition. His examination of white lead in the stacks is similar to the examination of the mineralogist who selects pure crystals, which he analyzes and finds to have definite composition. Other formulæ for white lead have been suggested, but apparently only by those who have analyzed commercial samples and who have not been familiar with the process itself. It is true that commercial white leads may contain a higher percentage of carbonate of lead than that shown by the theoretical formula; this is due to the fact that the corroding operation is not under complete control. At times, carbon dioxide will be in excess, and it will then, in the conditions in which the white lead exists, act upon the white lead, converting it to neutral carbonate.

There is no evidence that a limited excess of carbonate of lead in white lead is objectionable. Some advocate a percentage higher than the theoretical. It would appear proper, however, that some reasonable limit should be placed upon this excess. What this limit should be can be determined only by thorough physical and practical tests.

It is apparent then, that white lead cannot be considered as a mechanical mixture of carbonate and hydrate of lead. It is possible that hydrate of lead can be mixed with carbonate of lead, and be made to combine, but there is no evidence that the properties of white lead are the properties of carbonate of lead and hydrate of lead separately considered.

The question has arisen as to the proper chemical name for white lead. It may be questioned as to whether it is desirable in all or many cases to use chemical names for commercial products. Commercial products are seldom approximately composed of a single pure chemical constituent, and by using a chemical name for a commercial product we presuppose approximate purity. Chemists, of course, in making their analysis, obtain chemically pure precipitates, but, in the case of mechanical mixtures, the results obtained by analysis are of value in proportion as they are expressed in percentages of the original proximate constituents and, in so far as possible, in commercial terms.

Now especially is this true in the case of white lead, for in the writer's opinion, there is no thoroughly satisfactory chemical name current for even pure white lead. The most common name is "basic lead carbonate" but this is not satisfactory in that it is not sufficiently descriptive. It is possible to have anhydrous basic compounds. The name "hydrated basic lead carbonate" is equally unsatisfactory, for the reason that the word "hydrated" may refer to water of crystallization, as in the case of so-called "fully hydrated calcium sulphate." Probably, the best

name for chemically pure white lead is "lead mono-hydrate dicarbonate," which is exceedingly cumbersome and not likely to be substituted for the simple name white lead, which will probably continue to be used as answering all practical purposes.

The Value of White Lead as a Pigment. That white lead is the only white pigment which has been generally and successfully used, at least in this country, as a pigment by itself is a fact which requires no demonstration. Some of the reasons that have been assigned for this superiority of white lead are untenable. The commonest explanation advanced for the superiority of white lead is that it enters into combination with linseed-oil, forming a lead soap. It has been said that the hydrate of lead combining with the linseed oil in this way gives to white lead paint its working qualities and, as a supplement of this theory, it has been asserted that it is the carbonate of lead that gives to white lead its body. So many eminent authorities have accepted and advocated this theory that we feel some hesitancy in questioning it. It would appear, however, that there is little ground for the belief that white lead combines with linseed oil, except to an almost inappreciable extent. Hanney pointed this out many years ago when he found that by the extraction of white lead paste he was able to obtain practically all of the linseed oil it contained in its original form. Hanney's work has been duplicated by the writer on many occasions, confirming his results and conclusions.

It is true that white lead can be made to react on linseed oil at about the temperature of boiling water, but even then the reaction is only slight, unless the heating is prolonged for some time. White lead contains about 31 per cent of lead hydrate. Figuring from the saponification value of linseed oil, which we place at 190. 100 lbs. of white lead would require 76 lbs. of linseed oil to combine with this lead hydrate. It is seen, therefore, that, in a white lead paste containing 10 per cent of linseed oil, there is a large excess of base which would insure the complete saponification of the oil if such a reaction should take place.

On extracting white lead paste with ether, it is found that the linseed oil obtained contains a very small percentage of lead. The lead soaps obtained by precipitating the fatty acids of linseed oil with a lead compound dissolve readily in ether, with the exception of the lead soaps of the saturated fatty acids, so that practically all lead compounds would be dissolved by the ether. White lead adds to the drying qualities of linseed oil with which it is ground to the extent of this very small amount of lead, which combines with the linseed oil and dissolves in it.

As linseed oil paste does not show a combination of the white lead with the linseed oil, so it is also found that where an excess of oil is used there is no appreciably greater amount of combination

between the hydrate of lead present and the linseed oil. Whether there is any combination between oxidized linseed oil and white lead after a paint has been applied is not definitely known. We have, however, no evidence that such a combination takes place, and it seems improbable that it does.

The conclusion, then, is that white lead is a relatively inert pigment, entering into combination to only a slight degree, if at all, with linseed oil or any of its constituents, when mixed with it as a paint.

THE MANUFACTURE OF WHITE LEAD BY THE MODERN CARTER PROCESS

By Courtesy of Carter White Lead Co., Chicago, Ill.

CHEMICALLY, white lead manufactured by the Carter process is the same as when manufactured by the Old Dutch process. In each case pure metallic lead is converted into basic lead acetates which are acted upon by carbon dioxide to form basic carbonate of lead, or white lead.

The Carter process starts with pig lead, a grade commercially known as "corroding," which is as free as possible from bismuth, antimony and other impurities.

The first step is to atomize the metallic lead, the method being substantially the same as atomizing a liquid in the ordinary nasal atomizer. The pig lead is melted in a kettle to which is affixed a nozzle through which the molten lead flows by gravity. At the outlet it is struck by a jet of superheated steam which atomizes or blows the lead into very fine particles which are very slightly oxidized.

FIG. 194.

In some text-books on paints and paint pigments, the Carter process is referred to as "the quick process." This is a little misleading, for while the time of corrosion is cut down from about 120 days by the Dutch process to about fifteen days, the mass of metallic lead exposed to the corroding agencies is reduced in much greater proportion.

The powdered lead, in charges of about 4000 pounds, is then placed in wooden cylinders about 6 feet in diameter and 10 feet long, which revolve very slowly on their own horizontal axes.

The metallic lead in the cylinders is treated with dilute acetic acid (vinegar) and carbon dioxide (carbonic acid gas). A very weak solution of the acetic acid is sprayed into the cylinders at intervals. The carbon dioxide is admitted through the center of the head and is produced by the perfect combustion, in the presence of an excess of oxygen, of carefully selected coke. The coke is burned under boilers so as to utilize its caloric value. The lead in the cylinders is kept moist with water during

corrosion and a certain per cent of oxygen (air) passes into the cylinders with the carbon dioxide.

The action of the acetic acid upon an excess of metallic lead and lead oxide produces various basic lead acetates. The carbon dioxide acting on the basic acetates forms basic lead carbonate or white lead. The acetic acid, freed by the action of the carbon dioxide on the basic acetates, acts again on the excess of metallic lead and lead oxide and is again liberated, and so on in cycles until corrosion is complete.

As the cylinders, Fig. 194, slowly revolve, the pulverized lead is carried upward on the interior of the cylinder and rolls down to the bottom, exposing new particles to the corroding agencies. The heavy mass also performs most efficiently the functions of a tube mill in grinding the carbonate off the metallic particles as fast as it is formed and reducing it to an exceedingly fine powder.

By the Carter process corrosion is complete in about fifteen days. No artificial heat is required, sufficient heat being generated by the chemical combination to keep the contents of the cylinder at about 145° F. during corrosion.

At the proper stage, the cylinders are emptied and the white lead is then washed and agitated in water, removing any traces of aectic acid or acetate of lead. It is then floated in water to remove the small particles of coarse lead, if any, and is then pumped into storage tubs, where the lead settles in the form of a heavy pulp. After evaporating the water from the pulp, you have commercial dry white lead.

For general use, white lead is put up in stiff paste form to facilitate mixing into paint. This paste consists of 92 per cent of hydrated carbonate of lead and 8 per cent of pure raw linseed oil. This paste is produced in two ways; one by chasing, mixing and grinding in a double set of heavy burr-stone mills, dry white lead and pure linseed oil; the other by mixing the lead pulp (lead and water) with linseed oil in what is known as pulp machines, the white lead taking up the oil to the exclusion of the water and becoming " lead in oil " which is then chased and mixed and run through the heavy burr-stone mills. The pulp process simply does away with drying the lead pulp, and the only purpose of the heavy grinding is to secure complete incorporation of the lead and the oil. Properly ground lead in oil, ground either dry or from pulp, does not contain more than 0.5 per cent of free moisture.

The last step in the Carter process is to convey the paste white lead from the mills to storage tanks, each of 75 tons capacity, where it is allowed to stand for several days before it is drawn off and filled into kegs. The pressure of the lead in these tanks completes a perfect saturation of the lead with the oil and forms a very smooth, unctuous paste.

XVII

SUBLIMED WHITE LEAD

S. M. EVANS

Vice-President Picher Lead Company, New York City

ONE of the recent developments in white lead pigments is a compound produced directly from lead sulphide ore by sublimation.

This product has lately come into very wide use under the trade name, "Sublimed White Lead." Chemically, sublimed white lead is entirely different from the the other white leads. Its characteristic ingredient is basic lead sulphate, which corresponds to the structural arrangement, $2PbSO_4 \cdot PbO$. This formula is analogous to the generally accepted arrangement of the basic carbonate molecule, $2PbCO_3:Pb(OH)_2$. Physically, it is amorphous in structure and, like other fumiform pigments, exhibits extraordinary fineness and uniformity of grain, the individual particles measuring about $^1/_{35000}$ of an inch in diameter.

The manufacture of sublimed white lead was begun in the lead-mining district of southwestern Missouri in 1870, and these factories, which were instituted by the inventor, E. O. Bartlett, have so far been the only ones which have been able to produce the pigment in a form acceptable to the paint trade. In Great Britain, where efforts to replace lead carbonates by non-toxic materials have been the subject of Parliamentary encouragement, there has been marked activity in experimentation. Although a number of factories have been installed and large sums of money expended, the English sublimed white leads have not approached the perfection of the American product.

Preparation. The method of production employed in this country bears a general resemblance to that used for the production of zinc oxide direct from ores, but the lead process requires a much finer adjustment of furnace conditions. The furnaces employed are low, water-jacketed "stacks" provided with large air doors opening immediately above the charge level and fitted with tuyeres arranged to maintain oxidizing conditions upon the surface of the charge of coke. The open fire is kept in a state of incandescence and the charge of powdered sulphide ore is sprinkled upon it through feed doors. The combustion is energetic; indeed so much heat is generated that the large brick chambers into which the sublimate rises are continually white hot.

There is no preliminary reduction to metal and, in most cases, no fusion of the ore, the reaction being almost of explosive violence. The equation may be represented as follows:

$$3PbS + 11O = Pb_3S_2O_9 + SO_2.$$

From the furnace chambers the products of combustion are drawn by suction through a horizontal brick flue and thence through an elaborate settling and cooling system consisting of brick towers and, finally, of sheet-iron pipes. The large fans which supply the draft necessary to draw the "fume" from the furnaces are located between the cooling pipes and the screen system. The latter is of the ordinary "bag room" type commonly employed for the collection of sublimates, and consists of a series of connected hoppers having no outlet except through collars in their tops. Inverted bags of filter cloth are attached to these collars and are suspended from the roof of the "bag room." The action of the fans forces the mixed fume and gaseous furnace products into these bags, which filter out the sublimate and retain it on their inner surfaces, while the gases and water vapor pass through and escape.

All reactions are completed within the furnace chambers and the horizontal flue, but the pigment is at this stage contaminated with discoloring furnace dusts. These are, however, much coarser than the impalpably fine "fume", so that in floating slowly through approximately one thousand feet of settling chambers and pipes the impurities gradually subside, leaving the sublimate lighter in color, until at the fans it has the appearance of a brilliantly white smoke. When collected, by shaking the bags, the sublimate is ready for the market and is packed directly into casks.

By-Product. A certain amount of pig lead, due to reduction of a part of the ore charge, is produced as a by-product of the manufacture of sublimed white lead. This is recovered by employing the familiar device of a "fore hearth," wherein the metal is separated by gravity from the fusible slags of the furnace. In order to maintain uniform furnace conditions and avoid interruptions of the process of sublimation, the slag and metal are allowed to flow from the furnace continuously instead of being drawn off at intervals by "tapping."

Commercial sublimed white lead differs in composition from the theoretical formula of the basic sulphate, in that it contains a higher proportion of lead sulphate. This is probably due to a slow combustion of a small part of the gaseous sulphur dioxide within the flue and a combination of the resultant sulphuric anhydride with the lead oxide of the basic sulphate. It is stated by manufacturers that it is perfectly feasible to produce the theoretical compound, but that so far it has not proven commercially advantageous. American sublimed white lead contains a small amount of zinc oxide derived from sphalerite, which is commonly associated with native lead sulphide.

Constitution. The constitution of sublimed white lead is practically constant and varies only within narrow limits. Its average analysis is approximately as follows:

Lead sulphate	$PbSO_4$	75%
Lead oxide	PbO	20
Zinc oxide	ZnO	5

The lead oxide is not free lead monoxide (litharge), but is present in combination as basic sulphate. Chemically this pigment is a distinctly stable compound, a feature which renders it unique among white lead pigments in that it does not react with linseed oil and resists the discoloring action of sulphur gases. Its inertness toward the acids and glycerides of linseed oil insures freedom from disintegration and consequent "checking" and crumbling of the paint. Like other stable pigments of extreme fineness the sublimed white lead coat wears from the surface. It also exhibits chemical inertness toward other pigments mixed with it. This quality renders it very useful in the manufacture of colored paints containing chemically reactive tinting materials. Its fineness makes it especially desirable for the production of ready-mixed paints, because it remains in suspension in the vehicle under conditions where the mechanically ground pigments tend to settle out of the liquid portion and to form a compact layer in the bottom of the container.

Sublimed white lead, when used alone, makes a very soft coat which does not resist abrasive action satisfactorily and is somewhat permeable to moisture. For this reason paint makers customarily incorporate with it a proportion of zinc oxide to obtain a greater degree of hardness. This practice has become almost universal as a means of improving the wear of lead paints in general, and, unless carried to excess it is a distinct improvement. The amounts of zinc oxide used for this purpose vary in different factories, but the formulas most generally used contain between 20 and 30 per cent.

XVIII

PIGMENTS, OILS, AND PAINT

MAXIMILIAN TOCH,

Paint, Varnish, and Dry Color Manufacturer, New York City.

Historical. Painting as a decorative art goes back to very ancient times. We find that the aborigines decorated their persons with earth colors, and that the Egyptians used pigments for the decoration of their temples. In the ruins of the Temple of Karnak in Egypt there are still decorative paintings on the walls and on the pillars which are more than 3000 years old.

Application. Protective paint, by which is meant paint used for the purpose of protecting the surface to which it is applied, is relatively new. In Europe building construction was of such a character, and is largely so to-day, that paint is not used to any great extent on the exterior of dwellings. Only in a pioneer country like America where domiciles were made of wood, was it found necessary to apply an exterior coating to preserve the wood.

For decorative and preservative effect, we find more evidence of the early use of paint in England, than we do in any other country. There are items of expense in the reign of Edward I showing the use of paint as early as the year 1274.

Up to the latter part of the fourteenth century, however, oil painting for artistic purposes was not an exact art. To Hubert and Jan Van Eyck, two Dutchmen, belongs the credit of first having made public their manner of oil painting by means of pigment ground as near as we know in linseed oil.

It is a fact worthy of mention, that there is one painting in the National Art Gallery in the city of London by the brothers Van Eyck, which is in as perfect a state of preservation as if it had been painted yesterday.

Occasionally we hear a complaint that the pigments made nowadays are not as good as those that were made in former years, and the poverty of our pigments is the cause of the early decay of many of our paintings.

An error of this kind deserves correction, for the art of manufacture of colors has never reached a higher plane than it has at present, but to the ignorance of the painters and to the greed of paint makers must we attribute the fugitiveness of our paintings. As nearly as can be deter-

mined there existed between the twelfth and the seventeenth century, at most nine or ten pigments. To-day we have 215 or more, 200 of which ought never to be used for permanent artistic painting.

When we see a painter with a pot of paint and brush painting either a steel or wooden structure, we imagine without further thought that that is the use to which most paints are put. As a matter of fact, paints and colors are used in enormous quantities in the arts and sciences for purposes other than decorative or protective printing. The following is a list of the purchases of the Bureau of Engraving and Printing, Washington, D. C., for the year 1910, showing the actual contract for 1,599,900 lbs. of pigments:

White	802,200 lbs.
Black	297,500
Blue	52,000
Green	180,000
Red	68,200
Yellow	200,000
	1,599,900

These pigments are identical in every respect with those used for general painting, and yet all these pigments are used for the purpose of printing the currency and the postage stamps of this Government.

The printing ink industry in the United States consumes enormous amounts of paint. In some instances the paint is ground in a varnish made of linseed oil, but for book and newspaper ink linseed oil is not used, but resinous mediums which act as a binding material for the pigment.

The floor oil cloth and table oil cloth industries are also enormous users of paint in the strict sense of the word; and while it is true that the mixtures which they make differ from the house painters' mixtures, the principle involved is identically the same as that of ordinary paint.

The shoe and leather industries are users of paint materials in large quantities, for making patent and harness leather, and so is the wall paper industry, the window shade industry, the rubber industry, and the cement industry, all using for their color effects the same pigments that are used for ordinary painting.

In the strict sense of the word, paint which is used on concrete, steel or wood, is an engineering material, and serves a purpose which is far more valuable than we imagine.

The pigments used in ordinary general manufacture of paints are as follows:

White Lead. White lead is one of the oldest pigments known and was described by Pliny 400 B.C. White lead was made from the mineral cerusite which is a native carbonate of lead, but about 400 years

ago the Dutch found that when pig lead was submitted to the action of carbonic gas from rotted tan bark and manure in the presence of vinegar, the basic acid salt which was first formed was slowly converted into a hydrated carbonate. The same method is used to this day, but newer methods are also used, such as the precipitation of hydrated carbonate of lead from a solution of lead by means of carbon dioxide.

Lead Sulphate. Lead sulphate has very little value as a paint material owing to the fact that the sublimed white lead described in a previous chapter, supersedes it. Sublimed white lead is a furnace product made from the sublimation, at a very high temperature, of Galena or native lead sulphide and sphalerite.

Zinc Lead White. This is a sublimed mixture of lead sulphate and zinc oxide in about equal parts.

Zinc Oxide. Zinc oxide as a paint pigment is only fifty years old, and when it is taken into consideration that in that short space of time its use has grown until in 1905 nearly seventy thousand tons were used in the paint industry in the United States, it speaks for itself that the material must possess exceptional merit to have advanced so rapidly. At the same time, although it is impossible to obtain any exact figures on the subject, it is probable that more than one-half of this seventy thousand tons were used in connection with other materials.

The discovery of zinc oxide by Le Clair in France and Samuel T. Jones in America are sufficiently well known, and have been quite thoroughly written up in other books. The former made zinc oxide by subliming the metal; the latter made it by subliming zincite and franklinite ores. The specific gravity of zinc oxide will average 5.2, and 50 lbs. will take 50 lbs. of linseed oil; in other words to produce the proper mixed paint zinc oxide will require a far greater proportion of linseed oil than white lead requires. It is generally stated in text-books that zinc oxide is not affected by sulphur gases and therefore will not turn color. This statement is not exactly correct, the author having always contended that zinc oxide is not visibly affected by sulphur gases, but there is no doubt, as any chemist will admit, that zinc oxide is affected by sulphur gases, although not to the same extent as white lead. As zinc sulphide, zinc sulphite and zinc sulphate are white products, the absorption is not evident to the eye, and hence the erroneous statement has crept into use that zinc oxide is not affected by sulphur gases.

When mixed with linseed oil and the proper amount of drier it sets and dries much more slowly than white lead. Nevertheless this drying continues in the form of progressive oxidation until the surface becomes very hard. A comparison between zinc oxide and white lead paints will show that the progressive oxidation which takes place when white lead dries, produces a chalky mixture, while the reverse is true of zinc oxide, which will produce a hard and brittle, vitreous surface which is somewhat affected by temperature changes. Owing, therefore, to the

diverse effects of the two pigments, a combination of lead and zinc is often well recommended. The hard drying zinc has not, however, been very well understood. Fifteen years ago the author undertook a series of experiments and found that the drier was very largely responsible for the hardening action of zinc. If the linseed oil be prepared with litharge, (PbO), the resulting zinc paint will last far longer and be much more flexible and consequently not readily cracked when exposed to a variation of temperature of even 130°F, such as we have in this climate. If, however, a drier is used in which manganese, (MnO_2), and red lead, (Pb_3O_4), have been cooked with the oil, the action of the manganese continues until a vitreous surface is the result. It is owing to the result of these investigations that the use of American zinc oxide made from franklinite ore has become so general for the manufacture of white table oilcloths.[1]

When enamel paints are made of an oil varnish and zinc oxide, and the drier in the varnish is composed of manganese and lead, the enamels eventually become hard, evidently through the catalytic action of the manganese. It is desirable to omit the manganese in high-grade enamels, or, where manganese must be used, in order to obtain a rapid setting, the borate of manganese should be employed, but only in very small quantities.

The American zincs are: First. The *Florence Red* and *Green Seal* zincs, which are made by the sublimation of the metal, are practically pure and equal in all respects to those made in France and Belgium. Second. The New Jersey zinc oxides, which are made from franklinite ore, are free from lead and frequently run over 99 per cent ZnO. Third. Mineral Point zinc, which is made at Mineral Point, Wis., and contains from 2 to 4 per cent of lead sulphate. Fourth. The leaded zincs made in Missouri which contain from 4 to 10 per cent of sulphate of lead.

Zinc oxide chalks to some extent in the same manner as white lead, but only if the atmosphere is charged with carbon dioxide or salt. The same experiment which was carried out with white lead in order to show its solubility in a solution of carbon dioxide was carried out with zinc oxide and the same result obtained. Much weight cannot be given to these experiments, because these chemicals are not always present in the atmosphere. They are merely chemical results which demonstrate both the cause and the effect, but it is of some interest to know why the paint films perish. The zinc oxides made from western ores are slightly more permanent than those made from the New Jersey ores, and as paint materials they possess the advantage of containing a larger quantity of lead sulphate.

Nearly all zincs contain a small percentage of zinc sulphate. Much unnecessary trouble has been caused by the critisism against zinc sulphate. Where a pigment contains moisture or where water is added in very small amount to a heavy paint in order to prevent it from settling, and not more

[1] *Journal of Society of Chemical Industry*, No. 2, Vol. XXI, Jan. 31, 1902.

than 1 per cent of actual water is contained in the paint, zinc sulphate forms an excellent drier, particularly where it is desirable to make shades which contain lampblack. The outcry against zinc sulphate is unwarranted because as much as 5 per cent is used in making a patent drier. The amount of zinc sulphate, however, in most of the dry zinc pigments probably decreases with age. Zinc oxide or other zinc paint which will assay 1 per cent of zinc sulphate will, when kept in storage for six months, show decrease in the zinc sulphate to one-half of one per cent.

In enamel paints the presence of zinc sulphate is not a detriment, and in floor paints it might be considered as a slight advantage, for it aids in the drying and hardening. However, too much of the soluble salt is never to be recommended.

Lithophone. When solutions of zinc sulphate and barium sulphide are mixed together in molecular proportions, a heavy flocculent precipitate is formed according to the following reaction:

$$ZnSO_4 + BaS = ZnS + BaSO_4.$$

The theoretical percentage will be 29½ per cent zinc sulphide and 70½ per cent barium sulphate. This precipitate as such has no body or covering power, and when washed and dried is totally unfit for paint purposes, but John B. Orr, of England, in 1880 discovered that when it is heated to dull redness, suddenly plunged into water, ground in its pulp state, thoroughly washed and dried, its characteristics are totally changed, and it makes a very effective and durable pigment for paint purposes. In the first place, it is a brilliant white; in the second place, it is extremely fine in texture, and in the third place, it has the same tinctorial strength but more hiding power than pure zinc oxide. Inasmuch as it is a complete chemical compound it is stable in every medium known for paint purposes, excepting those which are highly acid. It took several years to perfect the manufacture of lithopone, but it may be said that at the present time lithopone is made with great uniformity and has valuable properties.

Lithopone is likewise very largely used in the cheaper grades of enamel paints, because it does not combine with rosin or semi-fossil resin varnishes and therefore remains unaltered in the package. As an interior white, a first coat white, a ready-mixed flat paint for surface, or as a pigment in the lighter shades for floor paints, lithopone cannot be excelled for its body, durability, hardness, fineness of grain, and ease of application. It does not oxidize progressively, and this single feature has made it invaluable to the table oilcloth and floor oilcloth industry throughout the world. Its indiscriminate use, however, is not to be recommended, and the paint chemist should be permitted to decide when its value is the greatest. As a marine paint, either as a first coat or for making neutral paints where other whites would be necessary, it is found to outlast both zinc oxide and lead carbonate.

Sublimed Blue Lead. In the sublimation of galena a peculiar sulphide of lead is produced, which has been known commercially as blue lead, on account of its blue-gray appearance. This product has been on the market for several years. The contention is that sulphur fumes do not affect it as they affect red lead. As a priming coat it has been well spoken of.

Quicksilver Vermilion. Quicksilver vermilion is the amorphous mercury sulphide which is normally black, but when made with sulphur in the presence of an alkaline solution, it becomes bright red.

Red Lead and Orange Mineral. Red lead and orange mineral are the red oxides of lead and are both chemically alike. Red lead, is, however, made by heating litharge, which is the ground oxide of lead, and orange mineral is made by heating white lead until all the water and carbonic acid are driven off.

Venetian Red. This is a ferric oxide containing gypsum in varying quantities, obtained by heating ferrous sulphate in the presence of calcium oxide.

Indian Red. Indian red is generally a very pure form of ferric oxide made by heating copperas or ferrous sulphate until it is converted into ferric oxide.

Permanent Vermilion. Permanent vermilion is usually orange mineral tinted with para-nitraniline.

Burnt Ochre and American Sienna. Burnt ochre and American sienna are analogous, being made of hydrated oxide of iron and clay ore burnt until the ferrous salt is converted into ferric.

Chrome Yellow. Chrome yellow is chromate of lead made by adding chromate of potassium or sodium to a basic lead nitrate solution. The precipitate thus formed is washed, pressed and dried.

Ultramarine Blue, Cobalt Blue. Ultramarine blue and cobalt blue may both be made from the natural minerals.

Ultramarine blue whether artificial or genuine is chemically the same, with the one difference that the genuine ultramarine blue is the powdered mineral known as lapis lazuli, and ordinarily is the blue known under that name, but the mineral itself is found at times in an impure state either admixed with slate or gang rock, or contaminated slightly with other minerals. The genuine ultramarine blue may run, therefore, from a very deep blue to a very pale ashen blue, in fact, the lapis lazuli which lies adjacent to the gang rock is ground up and sold under the name of ultramarine ashes, which is nothing more nor less than a very weak variety of genuine ultramarine blue.

From the standpoint of exposure to light or drying quality, the artificial ultramarine is just as good as the genuine, and the only advantage that the genuine has over the artificial is that the genuine is not so quickly affected by acids as the artificial is.

It may be of interest to know that in 1814 Tessaert observed the

accidental production in a soda oven at St. Gobain (France) of a blue substance which Vanquelin declared to be identical with lapis lazuli.

In the following year the same observation was made by Huhlmann (at St. Gobain, in a sulphate oven) and by Hermann in the soda works at Schoenebeck (Prussia).

In 1824 La Société d'Encouragement pour Industrie offered a prize of 6000 francs for the production of artificial ultramarine which, in 1828, was awarded to J. B. Guinet, a pharmacist of Toulouse, later of Lyons, who asserted that he first produced ultramarine in 1826. Vanquelin was one of the three " trustees " holding the secret contrary to the rule of the Société.

In December, 1828, Gmelin of Goettingen explained his process of making artificial ultramarine before the Académie des Sciences of Paris. He used as the basis a mixture of precipitated hydrate of alumina and silex, which was, later on, superseded by China clay (kaolin).

In 1829 Koettig produced ultramarine at the Royal Saxon Porcelain factory at Meissen.

In 1834 Leverkus, at Wermelskirchen and later at Leverkusen, on the Rhine, produced the pigment.

In 1837 Leykauf and Zeltner at Nuremberg, introduced the manufacture of ultramarine into Germany.

Prices of ultramarine in 1830:

Natural	\$50.25 per pound
Artificial	4.05 per pound

Ultramarine is composed of alumina, silica, soda and sulphur.

The ultramarine blue which is made by means of a potash salt instead of a soda salt has every analogy of color and shade to genuine cobalt blue except that the genuine cobalt blue is not affected by acids as rapidly as the artificial.

Prussian Blue. This is a very permanent and powerful color made by precipitating solutions of ferrous salts with ferrocyanide of potassium, and subsequently converting into the ferric condition.

Chrome Green. Chrome green is a mixture of chrome yellow and Prussian blue, and is not the chromium oxide described in the next paragraph.

Chromium Oxide. This green is one of the most permanent greens used, but it is not extensively employed in the manufacture of mixed paints except where absolute permanence is necessary. It is met with occasionally in railway paints for switch target signals, and as a mixed paint to be used on vessels for repainting the receptacle in which the port lights rest. It is not a brilliant green and cannot be compared with the chrome greens, which are mixtures of chrome yellow and Prussian blue. It is more of an olive shade.

Lamp Black and Carbon Black. Both of these are condensed soots, the one made from dead oil, and the other usually from gas. They are pure carbon.

Graphite. Graphite is either artificial or natural, and very seldom contains more than 90 per cent of carbon. It has a peculiar silvery luster by which it can be identified.

Charcoal and Coal. Charcoal and coal are analogous in composition, except that charcoal black is alkaline and coal black acid. Vine black is also the same as charcoal black.

Mineral Black. Mineral black is usually a slate colored with oxide of iron.

Silica and Infusorial Earth. Silica and infusorial earth are usually either ground quartz or the native infusorial earth washed and powdered. China clay and kaolin are silicates of alumina largely used as either reinforcing pigments or substratums for lakes.

Barium Sulphate. Barium sulphate is an artificial precipitate, usually made from barium chloride and sodium sulphate, and is largely used as a lake base, and in its dry form as a reinforcing pigment. The United States navy has lately experimented with it in a very large way for making battleship gray.

Barytes. Barytes has the same chemical composition as the artificial barium sulphate, but is the native mineral, finely powdered.

Calcium Carbonate. Calcium carbonate is either whiting, or white mineral filler or powdered marble.

Gypsum and Terra Alba. Gypsum and terra alba are either artificial or natural calcium sulphate.

Prince's Mineral and Prince's Metallic. Prince's mineral and Prince's metallic are both oxides of iron containing about 40 per cent of oxide, the balance being silicate or clay.

Ochre. Ochre is clay stained with the hydrated oxide of iron.

Umber. Umber is a clay earth stained with oxides of manganese and iron.

Sienna. Sienna is largely composed of hydrated oxide of iron and a very small percentage of clay.

Vandyke Brown. Vandyke brown is a clay earth stained with a bituminous compound.

Paint Vehicles. The vehicles or liquids used in making paint are linseed oil, soya bean oil, China wood oil, fish oil, corn oil, turpentine, benzine, benzol, turpentine substitutes and driers.

Linseed Oil. Linseed oil is the oldest paint vehicle known. It is the oil expressed from the flax seed, or, as it was formerly known, the linen seed, hence its name, linseed. Most of the raw linseed oil produced in the United States comes from the northwest. The foreign oils come from Calcutta, the Baltic, and the Argentine regions. The oldest method for extracting the oil consists in crushing the seeds, heating it in a steam

jacketed kettle and finally subjecting it to hydraulic pressure. In a later method, which is a continuous one, the crushed seed is forced through a screw press, the oil thus oozing through the openings in the bottom of the tube while the cake falls out at the end in the form of flakes. A third process consists in extracting the crushed seed by means of naphtha, the excess of solvent being subsequently removed by evaporation.

Linseed oil dries by oxidation and this may be hastened by the addition of salts of lead or manganese, known as *driers*.

Soya Bean Oil. Soya bean oil is closely allied to linseed oil, but there are some seventeen varieties of it, and most of them are very poor driers, and remain sticky for a long time. There are three or four varieties of soya bean which yield very good oil, but until these are scientifically cultivated it will be rather difficult to recommend them.

China Wood Oil. China wood oil has been known in America since 1896 only, and is known under the name of tung oil, kiri oil, and China nut oil. It cannot be used in its raw state, but must always be cooked, with the addition of a suitable drier, to a temperature of over 500° F. It makes a very waterproof material.

Fish Oil. There is only one variety of fish oil that is used in paint making, and that is known as menhaden fish oil, which is the oil extracted from the moss-bunker. The fish are collected on the northeastern coast of North America. When used up to about 70 per cent with other oils, it makes a suitable oil for paint purposes.

Corn Oil. Corn oil, as the name indicates, is the oil pressed from the seed of the corn or maize plant, and does not dry very well. When mixed with linseed oil it has some uses as a grinding oil.

Turpentine. Turpentine is one of the oldest solvents known. It is collected from the sap of the pine tree in the southern part of the United States, and when this sap is distilled it yields ordinary and spirits of turpentine.

Benzine. Benzine is a light fraction of petroleum oil or asphalt oil, and is more inflammable than turpentine. It has a very large use in the paint industry, particularly for the manufacture of oil cloth, linoleum, etc., where a cheaper solvent is necessary.

Benzol. Benzol is a light fraction derived from coal tar and has great solvent properties. It is a desirable constituent of mixed paint which is to be used for painting new wood, and if used up to a reasonable limit improves the spreading quality of paint considerably.

Turpentine Substitutes. There is a large class of turpentine substitutes which are replacing turpentine itself. These are the higher fractions of petroleum and asphalt oils which have about the same specific gravity as turpentine. They are much more reasonable in price, and in many instances serve the same purpose as pure turpentine.

Driers. Driers are needed in almost all paints. It is assumed that they exert no chemical action but attract oxygen from the air by virtue

of their presence. The principal driers used in paint making are made of soaps composed of lead and manganese in some form or other, usually as the linoleate or the resinate. Too much drier is regarded as harmful in paint, but a limited amount serves a very good purpose in that the paint is made to dry before dust can collect.

Mixed Paints.[1] In preparing paint from the above materials there are several methods employed. The most common procedure, however, is to mix the base with a small amount of the vehicle (usually linseed oil) in a suitable mixing machine. The oil is placed in the can of the mixer and the pigment added in small portions at a time, until the proper amount has been introduced. A thick paste should be the result of this operation, which on becoming homogeneous is passed through a powerful mill. The mills most commonly used are similar to the one shown in Fig. 10, and consist of two heavy burr-stones, which may be so set as to give any degree of fineness desired. The latest type of mill is provided with water cooling device so as to prevent overheating through the friction of the stones.

It is sometimes desirable to regrind the paint; this is accomplished by returning to the same mill, or as is more common, passing it by gravity to a second mill of the same type. The ground paint is next transferred to the liquid mixer where the thinner is introduced and thoroughly incorporated. The thinner used will vary with every make of paint, but a typical mixture would consist of raw linseed oil, turpentine, drier, and benzine, the amount of each depending largely upon the price and nature of the paint in question.

For some of the colored paints boiled linseed oil is substituted for the raw oil, owing to the fact that the boiled oil dries much more rapidly. For paints which are to have a high gloss a certain amount of varnish is usually added. When a large amount of turpentine is employed the paint dries with a flat surface. Flat finishes are also obtained by using treated China wood oil in the thinner. Owing to the high price of linseed oil, as well as the beneficial results obtained, it is quite common practice to add a certain amount of semi-drying oils as for example, soya bean oil, corn oil, fish oil, or other substitutes.

The benzine is added to hasten the drying by evaporation, while the drier is added to aid in the oxidation of the oil.

When the paint is properly thinned it is ready for shipment. As prepared in the above manner the paint is supposed to be ready for application, but as a matter of fact they should be too thick and should require a certain amount of further thinning before they are fit to use.

[1] Editor's note.

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XIX

"THE METALLURGY OF IRON AND STEEL."

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Iron is a metal and one of the commonest of the chemical elements on the earth's surface. From the magnetism of the earth we may also

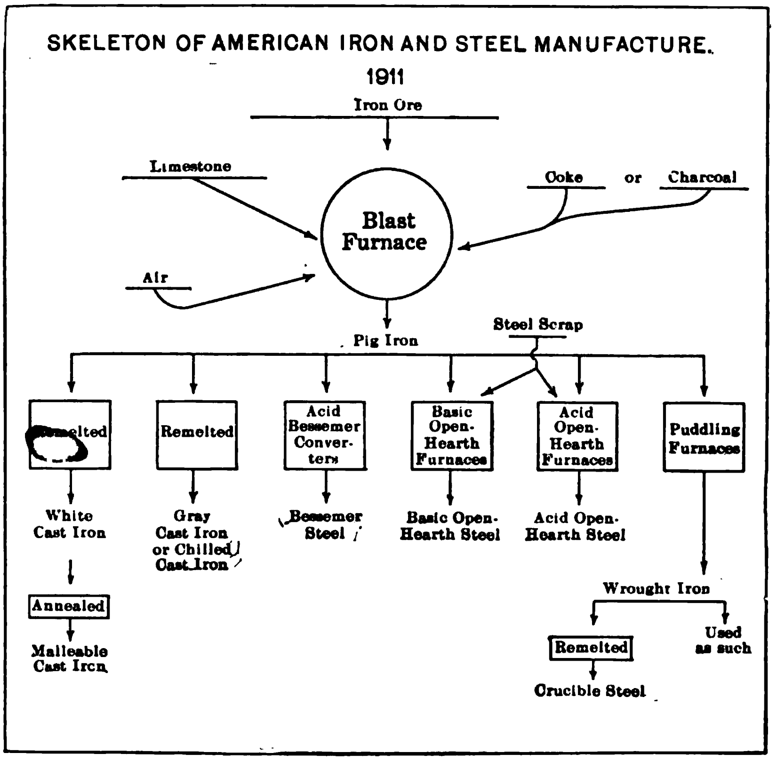

Fig. 195.

infer that its interior is probably an iron ball, and that the supply is limitless provided we can get at it. The most important chemical properties of iron from a practical standpoint are: First, its liability to oxidation in damp air (i.e., rusting); second, the ease with which its oxides (ores) are

reduced at all temperatures above 500° F. (260° C.), and third, its very powerful chemical affinity for carbon.

Its most important physical properties are its strength, magnetism, and ability to become hardened and to retain a durable cutting edge after appropriate manufacture and treatment. In these three properties it can be made to excel all other known substances. Add to them its cheapness, and we can understand the importance of the ferrous metals to industry and to civilization. Another characteristic of iron which is of almost equal importance is its very unusual adaptability. To illustrate this briefly: Iron can be made either the strongest or one of the weakest of metals; either the most magnetic or one of the non-magnetic metals; one of the hardest or one of the softest; one of the toughest or one of the most brittle; it may have a coefficient of expansion with changes in atmospheric temperature varying from almost zero to a maximum, and it may be given a combination of some of these different properties at will, according to the purpose for which it is to be fitted in service. And most of these variations are brought about by changing the amount of foreign elements by less than 5 per cent of the mass, or by giving it a different heat treatment, or by both together.

FIG. 196.—Blast Furnace and its Hot Blast Stoves.

Ores. The chief ores are the oxides, Fe_2O_3 and Fe_3O_4. In only a few localities is the carbonate important. Unless the proportion of

iron is at least 35 to 50 per cent, the ore can not be smelted with profit, except where the cost of mining plus mechanical concentration is low.

Blast Furnace. Over 95 per cent of all the iron ore treated goes into the blast furnace, where it is smelted with coke and preheated air,[1] and a relatively impure grade of metal, known as pig iron, is produced. The

Cross Section through Blast Furnace

FIG. 197.

modern American blast furnace conforms in a general way to the lines and dimensions of Fig. 197. A column of coke fills the body of the furnace from the bottom of the hearth to the top of the bosh, and above this are

[1] More rarely charcoal fuel and cold air are employed, and under certain conditions, a mixture of coke and anthracite, instead of coke alone.

alternate layers of coke and iron ore, together with an appropriate flux, which is generally limestone.

The preheated air, at a temperature of usually 800 to 1200° F. (425 to 650° C.) and at a pressure of about 15 lbs. per square inch, enters through the tuyere pipes at the top of the hearth, combines with the fuel and creates a volume of intensely hot reducing gases, which pass up through the interstices of the charge, melting, heating and reducing the ore which it meets, and finally passing out at the throat of the furnace. The temperatures at different points in the furnace and the various reactions which take place, are shown in a general way in Fig. 198. Below the top of the bosh the fuel is the only material not in liquid form. The iron, containing about 3.50 to 4.50 per cent of carbon and varying amounts of silicon, sulphur and other elements, according to the reactions of the smelting zone, collects in the bottom of the hearth, and on top of it the cinder, consisting of the impurities in the ore together with the ash of the coke and the lime, magnesia and impurities of the flux. All sulphur which is brought to the condition of CaS goes into the cinder, and all that in the form of FeS goes into the iron. With this exception the cinder contains all the oxidized materials and the metal all those in reduced condition.

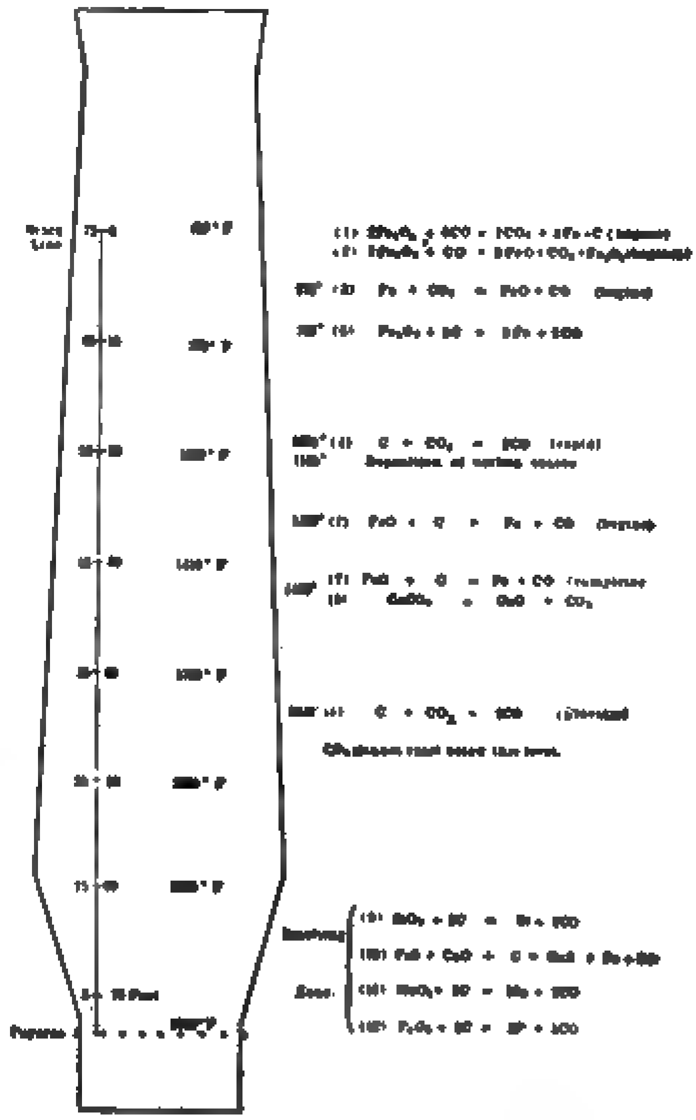

FIG. 198.

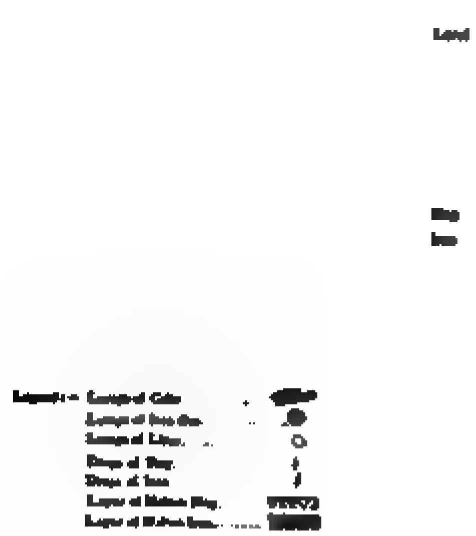

FIG. 199.

The cinder, because of its low specific gravity, floats on top of the metal and is drawn off about 15 times in twenty-four hours and disposed of. The metal is tapped out of the bottom of the furnace about every six hours and is either cast in the form of pigs or transported to a nearby steel mill in the liquid form.

The gas received at the throat contains about 22 to 27 per cent of CO and has a calorific power of 85 to 95 B.T.U. per cubic foot. About one-third of it is used for heating up the four hot blast stoves which preheat the air used for smelting, and the remaining two-thirds is consumed under boilers or in gas engines, for the generation of power.

Because of its impurity and therefore its friability, pig iron cannot be worked or wrought. Many millions of tons per year are used in the form of iron castings, and the remainder purified. The purification consists in oxidizing the carbon, silicon, and some other impurities.

FIG. 200.

Manufacture of Wrought Iron. In the puddling process, Fig. 200, the impurities are oxidized by melting pig iron on a bed of iron ore. The ore gives up its oxygen to the impurities and some iron is reduced from it.

$$Fe_2O_3+3C=3CO+2Fe$$
$$2Fe_2O_3+3Si=3SiO_2+4Fe$$
$$5Fe_2O_3+6P=3P_2O_5+10Fe$$

At the end of about one hour and a half the carbon, silicon and manganese are almost entirely eliminated, as well as a portion of the phosphorus and sulphur. The iron is then drawn from the furnace in a pasty state, because the heat is not sufficient to maintain it in the liquid form in a purified condition.[1] Wrought iron so produced is one of the purest of the iron and steel products. Its distinguishing characteristic is the webs and strings of slag mixed with it, which are drawn out by the rolling process, and give the metal its fibrous structure.

Crucible Steel. On account of its freedom from carbon, wrought iron lacks great strength and cannot be made to take a temper. If it be melted in crucibles with charcoal, pig iron, or some other substance rich in carbon,

[1] The purer the iron the higher the temperature at which it melts.

so that the resulting metal will contain from 0.75 to 1.50 per cent carbon, it makes a steel which is largely used for cutting tools and similar purposes, and is the highest in quality and price.

Bessemer Steel. Pig iron is also purified by the Bessemer process, Fig. 201, in which cold air is blown through a bath of liquid pig iron. The oxygen of the air oxidizes the silicon, manganese and carbon and these oxidized materials separate in the form of a slag, with the exception of the latter, which passes off as gas (chiefly CO). The complete purification of 10 to 20 tons of liquid pig iron requires only seven to fifteen minutes of blowing. The heat produced by the oxidation of the impurities is sufficient not only to keep the bath in the liquid condition during the operation but also to raise its temperature more than 575° F. (300° C.). The liquid metal, however, dissolves a good deal of iron oxide, which has a very harmful effect upon its qualities, but is nearly all removed by the addition of manganese at the end of the " blow."

FIG. 201.—A Bessemer Blow.

TYPICAL ANALYSES IN THE HISTORY OF A BESSEMER BLOW

Minutes from Commencement of Blow	Metal Bath.					Slag.					Escaping Gases.				
	C	Si	Mn	P	S	SiO_2	Al_2O_3	Iron Oxides.	MnO	Others.	CO	CO_2	O	N	H
Pig iron ..	4 00	1 00	0 50	0 090	0.070										
2........	4 10	0 70	0 15	0 093	0 071	50 0	6 0	2 0	5 0	37.0	. .	10 0	1 0	87 0	2 0
4..... .	3 50	0.35	0 05	0 095	0 072	55 0	5 3	28.0	5 0	6 7	5 0	8 0	0 5	84 5	2 0
6	2 00	0.03	0 02	0 095	0 073	65 0	4.0	21 0	5 0	5 0	20 0	2 0	.	76 0	2 0
8..........	0 90	0 03	0 01	0.097	0 074	70 0	3 0	18 0	5 0	4 0	30 0	1 0	.	67 0	2 0
10	0 05	0 02	0 01	0 098	0 075	67 0	2 5	23 0	4 0	3.5		.	.	.	.
After Recarburising .	0.55	0.10	0.90	0.100	0 070	65 0	2 3	17.0	14 7	1 0	..	. .		...	

The appearance of the "converter" flame gives an index by which the operation may be followed and controlled. When the oxidation of impurities is completed, the flame shortens, or "drops," and the blowing is discontinued. Then is added a predetermined amount of manganese to remove absorbed oxygen; silicon to

prevent gas bubbles or "blow-holes," and carbon to give the desired degree of strength or hardness, or both.

Fig. 202.—Section Bessemer.

Basic Bessemer. Acid Bessemer slags are rich in silica, and this prevents the elimination of phosphorus from the metal, because silica will force phosphorus out of the slag unless there is a great predominance of basic radicles present to unite with both silica and phosphoric acid. However, by using pig iron low in silicon, and also adding large quantities of lime to the bath in the converter, we may make a basic slag, which is retentive of phosphorus, and permits it to be removed after oxidixing, just as in the puddling process already mentioned. At the same time the lining of the converter is made of basic instead of acid materials lest it be attacked by the slag. The basic Bessemer process has not maintained a foothold in America because the supply of pig iron sufficiently rich in phosphorus has not been so abundant as to create the competition which produces low prices.[1]

Fig. 203.—Blast Furnace Blowing Engines.

[1] Because the silicon in the basic pig iron must be low, the phosphorus must be high (1.75 per cent or more) in order to supply the necessary heat.

Quality of Bessemer Steel. Bessemer steel is the lowest in price and poorest in quality, and in America this process is now rapidly giving way to the basic open hearth process, chiefly because the supply of ore from which to make pig iron suitable for the Bessemer process is yearly running lower. The great field of the Bessemer process has been in the manufacture of railroad rails, wire and pipe. For the two latter commodities it bids fair to retain its predominance for a time at least, because it is especially adapted to the manufacture of steel low in carbon.

Open Hearth Steel. The open hearth process depends upon Sir William Siemen's method of obtaining very high temperatures by the

Fig. 204.

regenerative system. By this means a bath of iron may be maintained in a liquid condition at any degree of purity. The open hearth process really consists in remelting old steel scrap with varying amounts of pig iron. After the charge is melted, the impurities are oxidized by the addition of iron oxide, usually in the form of ore or mill scale. It takes from three to four hours to melt and about an equal length of time to complete the purification.

Except in England, where large amounts of acid open hearth steel are made for ships, bridges and other structural purposes, the basic process is predominant. The basic furnaces are lined with magnesite or dolomite and the phosphorus as well as silicon, manganese and carbon, are oxidized to as low a point as may be desired. An important, although

somewhat uncertain, amount of sulphur is also carried into the slag in the form of calcium sulphide CaS.

Manganese and silicon must be added to the metal at the end of the open hearth process, as in the Bessemer process, but even under these conditions, basic open hearth steel is liable to contain dissolved oxide and also to be impregnated with gas bubbles or " blow-holes." For the best grades of structural steel and steel castings, the acid open hearth process therefore, maintains its importance, in spite of the higher cost of manufacture due to the price of low-phosphorous pig iron and steel scrap.

Duplex Process. The combination of the acid Bessemer and basic open hearth processes has recently become of much importance, because it enables us to get some of the rapidity of working, which is characteristic of the Bessemer purification, together with the elimination of phosphorus. The metal is usually first blown in a Bessemer converter until the silicon and manganese, and about one-half of the carbon, are eliminated, after which it is transferred, still in the liquid form, to the open hearth furnace where the remainder of the carbon and the phosphorus is oxidized.

Fig. 205.

Electric Iron and Steel. Electricity may be used as a source of heat in the melting of either iron or steel, and in localities remote from fuel supply and adjacent to other cheap sources of power, experiments of this nature have been made with commercial success. They have excited a great deal of interest, although the volume of production has not yet attained relative importance. It is believed, however, that electric melting will give a cheaper, and a higher grade of steel than the crucible process, and important developments in this field have already begun. Electric furnaces are also the only means of producing some of the " ferro-alloys " because sufficient temperature cannot be otherwise obtained.

By means of electricity, temperatures may be obtained, hitherto unattainable with fuel, and an operation may be conducted in a non-oxidising atmosphere. Therefore a duplex process, consisting of the purification of steel at a very high temperature in an electric furnace, subsequent to either the Bessemer or the open hearth operation, has resulted in

Fig. 206.—Pig Casting.

a superior quality of steel (on account of freedom from dissolved gases and oxides, phosphorus and sulphur) at a medium cost.

Malleable Cast Iron. Iron castings lack strength and ductility on account of the impurities contained, and more especially on account of the large flakes of graphite, which destroy the continuity of the metallic mass. On the other hand, steel castings are costly to make, not only because of the expense of purifying, but chiefly because of their relative

infusibility and high shrinkage in cooling. A between-product has therefore been developed to which the name of malleable " cast iron " has been given, because, although its composition approaches that of ordinary cast iron, it differs from it in having a limited amount of malleability. It also has greater strength than cast iron and a very moderate degree of ductility. Malleable cast iron is made by first making castings of white cast iron in which the carbon is usually under 3 per cent and all in the combined form. These castings are then maintained at a bright red heat for two or three days or more, which results in the carbon being precipitated in very minute flakes of graphite, known as " temper carbon." Temper carbon differs from graphite chiefly in the small size of its particles, and the characteristics of malleable cast iron are due to this difference and also, in lesser degree, to the circumstance that the amount of carbon and phosphorus is less.

The Constitution of Iron and Steel. Iron and steel are not simple bodies but are of composite structure, formed of aggregations of different crystals. The nature of their constitution may be best understood by applying the modern theory of solutions. Space does not permit of our expounding this theory here, but those who have mastered it will understand its expression in the diagram shown in Fig. 207. The upper V-shaped curve of this diagram represents the freezing of the various alloys, or, as we sometimes express it, their crystallization from the liquid state. The upper left-hand freezing point locus, *AB*, represents the crystallization of iron containing about 2 per cent of carbon in solid solution. The upper right-hand locus, *BC*, represents the crystallization of a compound known as cementite, having the chemical formula Fe_3C. The lower line, *aBD*, represents the freezing of the eutectic, which consists of a mixture of the solid solution before mentioned, and cementite. The ultimate analysis of this eutectic shows 95.7 per cent iron, 4.3 per cent carbon.[1]

The lower V-shaped curve represents the decomposition of the 2 per cent solid solution of iron and carbon previously referred to. The line, *GOS* is the locus of the precipitation of pure iron (to whose crystals the name of ferrite is given). The line, *Sa,* is the locus of the precipitation of cementite, Fe_3C. The horizontal line, *PSK*, is the locus of the formation of what Professor Howe has very aptly called the " eutectoid," consisting of 7 parts by weight of ferrite and 1 part by weight of cementite and showing on ultimate analysis about 0.90 per cent of carbon.

It is to be remarked that the ordinate extending through the point *a* is especially chosen as the boundary line between steel and cast iron. In other words, all the alloys to the left of the point *a* (that is to say, all those with less than 2.20 per cent carbon) are classified as steel, and all

[1] Those who have not mastered the modern theory of solutions should refer to Howe's "Iron, Steel and Other Alloys" and to later researches on Metallography given in the list of references.

those to the right of this point are classified as cast iron. It will be noted that the foregoing paragraphs do not allow for the presence of graphite in cast iron. The occurrence of this metalloid has been the source of much research and discussion for which we have not space here. Suffice it to say that, in gray cast iron, the cementite which should be present according to the considerations mentioned above, is replaced in part (and sometimes in very large part) by graphite. This applies not only to the cementite theoretically born during solidification, but also that which is born in region *SaDK*, and during the formation of the eutectoid designated by line *PSK*. The presence of silicon in cast iron is one of the strongest

100% IRON 99% 95%

Fig. 207.

factors in promoting the presence of graphite instead of cementite. Rapid cooling from the liquid state on the other hand will tend to counteract this effect of silicon and produce an iron in which the carbon is in the form of cementite, or else is held in solid solution.

From the foregoing explanation we may observe that the iron alloys with less than 0.90 per cent carbon [1] consist of ferrite and the eutectoid.[2] The alloys between 0.90 per cent and 2.20 per cent carbon [3] will consist of pearlite and cementite. From these two classes graphite is not only theoretically absent, but in fact seldom occurs there. The alloys contain-

[1] That is, wrought iron, soft steel, structural steel, machinery steel, railroad rails, and even a great majority of spring steel.

[2] The name of "pearlite" is also given to the eutectoid.

[3] Comprising chiefly the steels used for cutting tools.

ing more than 2.20 per cent carbon include the whole class of cast irons, which will be termed " gray cast irons " if they contain 1 per cent or more of graphite, and " white cast irons " if their carbon is practically all in the form of cementite, or in the dissolved condition. When they contain but a fraction of a per cent of graphite, the cast irons will have a white surface on a freshly-broken fracture, with gray spots here and there, and to them is given the name of " mottled cast irons."

Properties of Ferrite. Ferrite is a weak, but very tough and ductile substance, having a high magnetic power and a relatively high conductivity for electricity as compared with the other constituents in iron and steel. We conceive that the weakness of ferrite is due in part to the large size in which its crystals ordinarily occur, and that this size is due in turn to their opportunity for growth, because they are born at a bright red heat in a relatively mobile mass. We come to this hypothesis because rapid cooling from just above the line *GOS* will not only decrease the size of the crystals of ferrite, but will greatly increase the strength of the iron.

Properties of Pearlite. The eutectoid is characterized by a very minute crystal size, so that high powers of the microscope are ordinarily necessary to discover its component crystals. This minute size is probably one of the reasons why steel with 0.90 per cent carbon has the greatest strength of all the normal slowly-cooled iron and steel alloys.

Properties of Cementite. Cementite is very brittle and hard, scratching glass with ease. It is magnetic but not nearly as strongly so as ferrite, and it is very fragile under shock. It is naturally of great service in cutting tools; but only within limits, because an excess renders the tool too fragile to bear the shocks of service. It is also useful for surfaces to resist abrasion, and on this account, the treads of cast iron freight car wheels, parts of rock-crushing machinery, etc., are locally chilled in order to rapidly cool them and produce white cast iron.

Properties of Austentite. Austentite is the solid solution of carbon in iron to which we have referred. The upper limit of carbon is about 2 per cent, although, by rapid cooling from the liquid state, and other abnormal means, we may greatly increase the amount of carbon retained in solution. The lower limit of carbon is, of course, zero. Austentite is hard, but not as much so as cementite, and it is also strong and brittle. As previously described in connection with the diagram, austentite has no normal occurrence in steel at atmospheric temperatures, but is completely decomposed into pearlite at about 1300° F. (700° C.), when the reactions on cooling are normal.

Properties of Graphite. Graphite is a soft substance, occurring in broad thin flakes which are themselves composed of thinner flakes, each having but slight adherence to the other. The chief effect of graphite in iron is to make it friable, weak and non-ductile. The weakening effect of the graphite is roughly in proportion to its amount, and also to the size of the individual flakes.

Effect of Combined Carbon on Iron. Combined carbon increases the strength of steel up to about 0.90 per cent, after which it has a weakening effect. It decreases the ductility, toughness, malleability, magnetic power and electric conductivity; increases the hardness both before and after quenching, and increases the brittleness.

Effect of Other Common Constituents. Manganese is added to steel for the purpose of removing dissolved oxide and also for neutralizing the harmful effect of the oxygen which it is not able to remove, as well as that of sulphur, because oxide and sulphide of manganese are not as harmful to iron and steel as the oxide or sulphide of iron. Sulphur increases the "red-shortness" of iron and steel, i.e., their brittleness at a red heat and phosphorus increases the "cold-shortness," especially when the metal is subjected to shock. The upper limit of sulphur and phosphorus in steel should be 0.10 per cent and in high grades it is customary to specify that these elements shall be below 0.035 per cent. Silicon and aluminium are added to prevent the retention of gas bubbles or blowholes in steel. Silicon is also added to cast iron in order to precipitate the carbon in the graphitic form, or to "soften" the metal as it is called. In this respect it is opposed by the action of sulphur which tends to produce white cast iron.

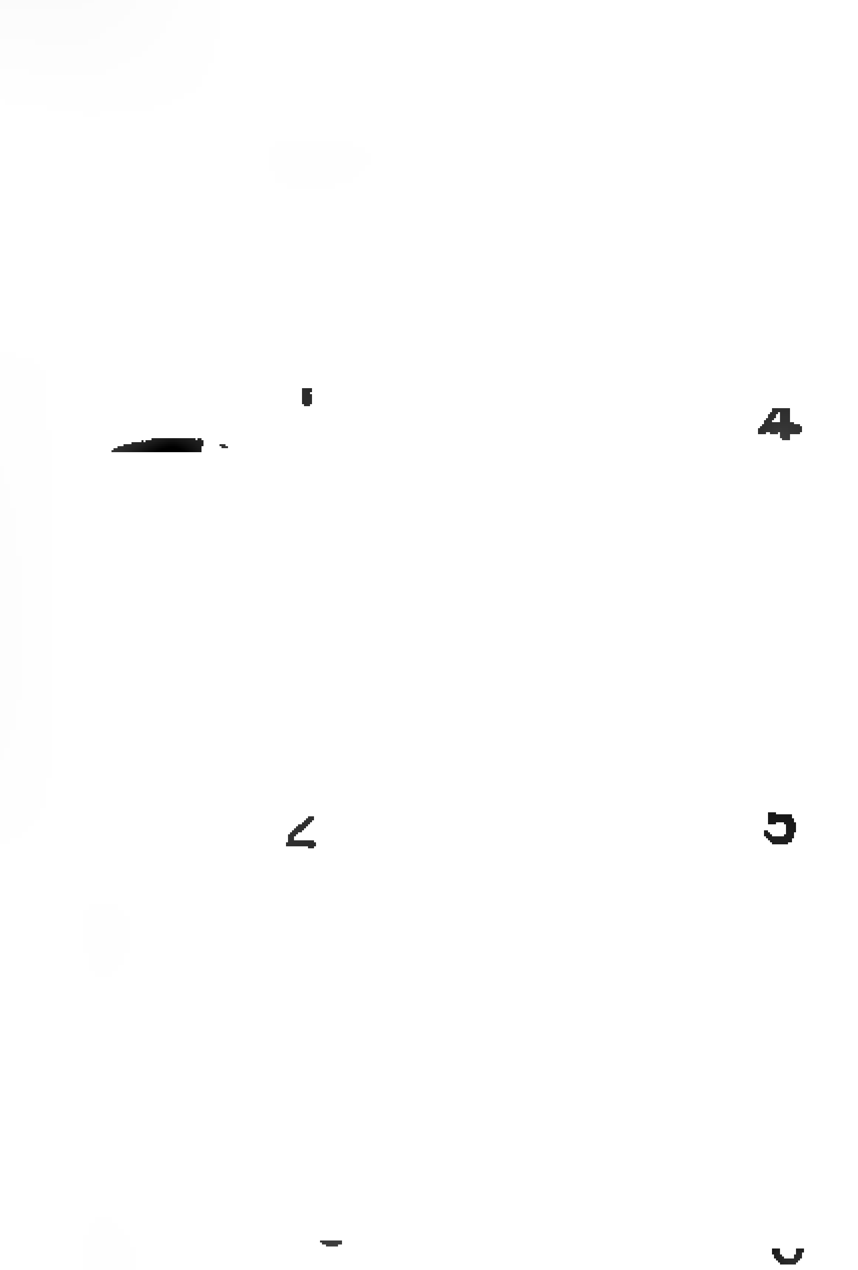

Fig. 208.

1. Electrolytic Iron; mostly Ferrite. 2. Steel of 1.50 per cent Carbon Cementite and Pearlyte. 3. Bubbles of MnTi in Steel. 4. Steel of 0.30 per cent Carbon Ferrite and Pearlyte. 5. Spiegeleisen $(Mn_3Fe)_3$ C and Pearlyte. 6. Phosphorus Eutectic, Fe_3P and Iron.

Titanium and Vanadium. Titanium is the newest element commonly added to iron and steel and it seems to have a powerful influence in removing the last trace of dissolved oxygen and nitrogen, as well as increas-

ing the fluidity of entangled oxides and slag in steel castings and ingots which enables these impurities to separate more easily from the mass. Titanium has already proved very beneficial in its addition in proportions of a few tenths of a per cent to railroad rails, and appears to have a beneficial effect in chilled cast iron and cast iron generally. Vanadium also appears to have a powerful effect in removing dissolved oxygen and seems to confer great strength on steel when used in combination with nickel or chromium.

Nickel Steel. The addition of nickel to steel in amounts up to 3½ per cent increases its strength and elastic limit without, at the same time, decreasing the ductility as much as would be the case if the additional

FIG. 209.—Effect of Heat Treatment.

strength were obtained by increasing the carbon. Nickel also reduces the rusting of steel and the segregation, and increases the soundness. Nickel-steel with 42 per cent of nickel has proven invaluable for certain measuring instruments, surveyor's tapes, pendulums, etc., because it is practically without expansion or contraction with changes of atmospheric temperature. The alloy with 37 per cent nickel has the same contraction and expansion with atmospheric temperature changes as has platinum and glass.

Manganese Steel. Steel with 12 to 15 per cent of manganese and in the neighborhood of 2 per cent of carbon is very resistant to wear and so hard and tough that it has proved very advantageous for railroad rails on curves, parts of rock-crushing machinery, burglar-proof safes, smaller sizes of armor-plate, etc. This material is very brittle when slowly cooled but, on heating to nearly a white heat and plunging into water, it becomes tough and ductile. thus reversing the ordinary effects.

Chromium Steel. Chromium is added to steel in amounts not more than 1½ to 2 per cent for the purpose of intensifying the hardness produced by heat treatment. It is very useful for such purposes as armor-plate, armor-piercing projectiles, parts of crushing machinery, etc. The combination of chromium with nickel, or with vanadium, together with special methods of heat treatment, such as double quenching, oil treatment, etc., produces a chromium steel with enormously high tensile strength.

High Speed Steels. Tungsten or molybdenum, when added to steel in proper proportions, produces a material which so greatly increases the efficiency of cutting tools as to have revolutionized machine shop practice and equipment. These steels are known as " high speed steels " because they do their cutting work so rapidly that the point of the tool may actually become a dull red through the heat of friction without losing its efficiency, and will last a longer time between grindings. The amount of tungsten in these steels is usually between 14 and 20 per cent, or else the amount of molybdenum will be between 6 and 12 per cent, while the carbon will be about 0.60 per cent.

Silicon Steel. Sir Robert Hadfield, the inventor of manganese steel, has also given us another alloy steel which has proven unusually efficient in magnets, because of its high permeability and high electric resistance. His patent covers the steel alloys containing 1 to 5 per cent of silicon, and the smallest possible amounts of carbon, manganese and other impurities. The steel is ready for use after a double (and sometimes a triple) heat treatment.

Heat Treatment of Steel. Under the " Constitution of Iron and Steel " we have mentioned that austentite, when slowly cooled, will break up into a conglomerate of pearlite, with either ferrite or cementite, this action taking place at about 700° C. (1292° F.). The chemical reaction is not an instantaneous operation, however, and may be prevented in part by rapid cooling from above this temperature down to atmospheric temperature. Since austentite is much harder and stronger than its products of decomposition, the hardness of this treated steel may be controlled by the rate of cooling, such as quenching in ice water, warm water, light oils, heavy oils, etc., or else we may quench in water in the first instance and then " temper " the intense hardness thus produced by reheating the steel to temperatures varying between 220 and 330° C. (430 and 625° F.). At these low temperatures steel takes on a variety of colors due to the thin film of oxygen which forms, and it deepens from a light straw at 220° C., to a deep blue at 320° C. These are known as the temper colors.

Corrosion of Iron and Steel. The corrosion of iron is its greatest weakness from the industrial standpoint and involves a loss of millions of dollars each year. A great difference of opinion exists as to whether steel or wrought iron rusts the faster, but it is now generally understood that the difference between these two materials is not great, if both

are well made. There is, however, a great superiority in well-made over badly-made material of either class. Steel which contains entrained slag, manganese oxide, iron oxide, much occluded gases or blow-holes, or in which the impurities are segregated, will yield more rapidly to rusting; and wrought iron, which contains an excessive amount of slag, not thoroughly worked, or which is irregular in composition, due to incomplete puddling or to the mixture with it of steel scrap during the welding process, or which has been made from low-grade scrap without remelting, will rust faster than well-made material. In short, it is now recognized that the quality of manufacture has a much greater effect than the process of manufacture. The old carbonic acid and hydrogen peroxide theories to explain the corrosion of iron, have now been replaced by the electrolytic theory, and it is recognized that any irregularity in the composition of the metal which produces a difference of potential, will hasten the rate of corrosion. There is also found to be a very great difference in the protective power of different paints and other coatings such as galvanizing, tinning, oxidizing, etc., for which the reader is referred to the recent treatise by Cushman and Gardner.

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XX

FERTILIZERS

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Historical. As far back as records go, the value of animal manures has been recognized in the growing of crops. Why they were of benefit and what relation their constituents bear to those of plants, are matters that have only been worked out during the past century. The earliest record of the use of mineral fertilizers is contained in a paper by Sir Kenelm Digby and printed in England in 1669. In this paper the use of saltpeter as a stimulant to plant growth is advocated. In 1804, Theo. de Saussure pointed out the significance of the ash of plants, and showed that without it plant life was impossible. Justus von Liebig in 1840 and 1842 was really the first practically to lay down the foundation of present fertilizer practice. By the middle of the nineteenth century the importance and value of nitrogen, phosphoric acid, and potash was pretty well known and it is from this time that the real growth, both of the use and knowledge of commercial fertilizers, dates.

Nitrogen as a fertilizer was first obtained from saltpeter and phosphoric acid was first derived from bones. Later nitrogen was obtained from by-products of slaughter houses and from ammonium sulphate, which is a by-product of coke-oven plants. Phosphoric acid was also obtained from petrified bone and from mineral phosphate beds in various parts of the world. The main source of potash at the present time is from the mines of Stassfurt, Germany.

Fertilizer Materials. Broadly speaking, there are two kinds of fertilizer materials: those which are in themselves a direct source of plant food, and those which, by their action, tend to make plant food fertilizers more available. While crops may grow without the use of fertilizers of the second class, no crops can mature without fertilizers of the first class.

Fertilizers of the second class comprise lime, gypsum, and common salt; they are all useful, but rarely indispensable. These are sometimes called "stimulant fertilizers." They tend to make rapidly available the stores of ammonia, phosphoric acid, and potash naturally present in the soil. When stimulant fertilizers are used exclusively for a term

of years, the soil loses ammonia, phosphoric acid, and potash. The inevitable result of such treatment must be finally the exhaustion of these important food constituents of the soil.

True fertilizers contain forms of plant food which contribute directly to the growth and substance of plants. Such materials may contain either ammonia, potash or phosphoric acid compounds, or all three.

Terms Used in Analysis. Fertilizer dealers and experiment station bulletins treat the different forms of fertilizer materials separately, and a familiar understanding of these trade names is important.

Ammonia is expressed either as nitrogen, as ammonia, or as nitrogen "equivalent to ammonia." There are various conditions in which phosphoric acid may be expressed such as reverted, available, insoluble, total, and phosphoric acid "equivalent to bone phosphate of lime." [1] Potash is expressed as potash, as potash actual, or as potash equivalent to sulphate of potassium or to chloride of potassium.

All genuine commercial fertilizers owe their value to the kind, quality, and amount of nitrogen, phosphoric acid, and potash they contain. They are made by mixing more or less of the several kinds of raw materials furnishing the desired ingredients, and to these may be added sulphuric acid to render the phosphoric acid available and a filler to make up the desired formula.

Nitrogen (Ammonia). Nitrogen is a gas, and in this form cannot be used in fertilizers; therefore, whenever we speak of nitrogen in fertilizers we do not mean that nitrogen exists in them as free nitrogen. The nitrogen in fertilizers is always combined with other elements and may be present in one or more different forms, such as nitrate of soda, sulphate of ammonia, or in the form of organic nitrogen as found in animal matter, such as blood, tankage, guano, or in vegetable matter, such as cotton-seed meal. Chemical analysis according to official methods does not really attempt to differentiate between the various forms other than to state whether or not the nitrogen in them is available. When, therefore, nitrogen is expressed in an analysis or guarantee as "ammonia" it refers to the entire amount of nitrogen present calculated as ammonia without regard to the form in which it is present. Ammonia consists of nitrogen combined with hydrogen and is also a gas and does not exist in fertilizers as such but in combination with other elements. Nitrogen equivalent to ammonia simply means that the total nitrogen content of the fertilizer is calculated to ammonia.

Phosphoric Acid. This as used in fertilizers does not exist as true phosphoric acid, but as various salts of phosphoric acid and lime. Soluble phosphoric acid is the mono-calcium phosphate formed during the process of acidulating phosphate rock or bone. Reverted phosphoric acid is the dicalcium phosphate which is also formed during the process of acidulation and is soluble in neutral ammonium citrate. Available phos-

[1] Phosphoric acid as used by the trade is not H_3PO_4, but the pentoxide (P_2O_5).

phoric acid is the sum of the soluble and reverted forms and is the total phosphoric acid in a condition capable of being absorbed by plants.

Insoluble phosphoric acid is the tricalcium phosphate as it exists in phosphate rock and bone and is not available for plant food. Total phosphoric acid is the total amount present irrespective of the form in which it is present. It is the sum of the above three forms. Phosphoric acid equivalent to bone phosphate simply means the total phosphoric acid calculated as the tricalcium phosphate.

Phosphatic Crude Stock.

Furnishing insoluble phosphoric acid:	*Furnishing available phosphoric acid:*
Animal:	Animal:
Bones	Dissolved bone, acid-fish-scrap.
Mineral:	Mineral:
Apatite, phosphate rock from Florida, Tennessee, of blue, brown and white colors.	Acid-phosphate from any form of mineral phosphate.
Thomas Slag.	

Potash. This term as applied to fertilizers always means the oxide of potassium. It is not found as such in fertilizers, but as either chloride, sulphate, nitrate or carbonate of potassium, or as organic potash.

Potash soluble means the actual K_2O soluble in water and is the only kind considered in fertilizers.

Crude Stock Furnishing Potash. Muriate or chloride, kainit, containing both muriate and sulphate; sulphate; double manure salt; the double sulphate of potash and magnesia; less important salts are carnalite, krugite, sylvanite. Carbonate of potash, such as wood ashes. As organic potash, tobacco stems and ashes, cotton-seed meal. As nitrate, potassium nitrate.

Geological Definitions. The primitive earths are four—clay, sand lime, and magnesia. Clay is called by geologists alumina, alumine, or argillaceous earth. Sand is called silex, silica, silicious earth or earth of flints. Lime as it exists in the soil is commonly called calcareous earth. The term calcareous is not properly applied to any earth unless it will effervesce with acids. Each of these earths answers a determinate and specific purpose in the economy and growth of plants, and the perfection of soil lies in a mixture of the whole.

Bases of the soil are: the primitive earths which enter into its composition; vegetable matter: all vegetable substances in a decaying or rotten state; animal matter: all animal substances in a putrefying state; organic matter: a term applicable to both animal and vegetable substances in a putrefying condition.

Vegetable mould: the earthy remains of vegetable substances which have either grown and decayed in the soil or have been conveyed thither in the progress of cultivation.

Loam is a combination of vegetable mould with the primitive earths. *Marl* is a substance consisting of lime with a small portion of clay, and sometimes of peat with a marine sand and animal remains. It is useful as manure, and is distinguished by shell clay and stone marl.

Expression of Formulæ. One often sees formulæ expressed in this manner, 4–8–2, or 3–6–4. It means that nitrogen comes first, phosphoric acid next, and potash third, hence the 4–8–2 indicates a fertilizer containing 4 per cent of nitrogen, 8 per cent of phosphoric acid, and 2 per cent potash. These figures multiplied by 20 give for each ton 80 lbs. nitrogen, 160 lbs. phosphoric acid and 40 lbs. potash.

Explanations of Market Quotations; how to Estimate the Value of Fertilizers. Phosphate rock, kainit, bone, fish-scrap, tankage, and some other articles are commonly quoted and *sold by the ton.* The seller usually has an analysis of his stock, and purchasers often control this by analysis at time of the purchase.

Acid phosphate is usually quoted at so much "per unit" of available, that is, soluble and reverted phosphoric acid. The meaning of the term unit is explained below. Tankage is usually sold with a quotation of so much "per unit of ammonia" and "per unit of bone phosphate." The amount of bone phosphate may be calculated by multiplying the amount of phosphoric acid by 2.1850. On the other hand, the amount of phosphoric acid is calculated from the bone phosphate by multiplying the latter by 0.4576.

Sulphate of ammonia, nitrate of soda, and the potash salts are quoted and *sold by the pound,* and generally their wholesale and retail prices do not differ materially.

Blood, azotin, and concentrated tankage are quoted at so much "per unit of ammonia." To reduce ammonia to nitrogen, multiply the per cent of ammonia by 0.8228; to make the reverse calculation multiply by 1.2154. A "unit of ammonia" is 1 per cent, or 20 lbs. per ton. To illustrate: if a lot of tankage has 7 per cent of nitrogen equivalent to 8.50 per cent ammonia, it is said to contain $8\frac{1}{2}$ units of ammonia, and if quoted at $2.25 per unit, a ton of it will cost $8\frac{1}{2}$ times $2.25, or $19.13.

Tankage and fish-scrap are sometimes sold at a price, based on analysis, with regard to both the nitrogen and phosphoric acid which the product in question contains. For example: Tankage, 9–20 quoted at $2.49 and 10 cents per unit, means that a given lot of tankage contains somewhere in the neighborhood of 9 per cent ammonia and 20 per cent bone phosphate, and is offered at $2.49 per unit of ammonia and 10 cents per unit of bone phosphate. A unit of ammonia, 20 lbs. is equivalent to (20 times 0.8228) 16.46 lbs. of nitrogen and is quoted at

\$2.49. One pound of nitrogen, therefore, costs $\frac{2.49}{1.65}$ equal to 15.10 cents.

A unit of bone phosphate, 20 lbs., is equivalent to 20 times 0.4576 equal to 9.15 lbs. of phosphoric acid, and is quoted at 10 cents. One pound of phosphoric acid therefore costs $\frac{10}{9.15}$ equal to 1 cent.

Hence it appears that a tankage containing 9 per cent ammonia and 20 per cent of bone phosphate and quoted at \$2.49 and 10 cents per unit, costs for nitrogen 15.1 cents per lb. and for phosphoric acid 1 cent per lb.

The cost of such a tankage will be 9 units of ammonia at \$2.49 equal. to \$22.41 plus 20 units of bone phosphate at 10 cents per unit, or \$2.00 or \$24.41 per ton.

Soil. Soils are generally divided into three groups: clay, loamy, and sandy. These in turn are subdivided as their general characteristics approach each other, thus:

Clay	Heavy clay Medium clay Loamy clay
Loamy	Clay loam Loam Sandy loam
Sandy	Loamy sand Sand

There are also other distinct forms, such as limestone, peaty and gravelly soils, but those given above best serve to describe the general conditions of farming lands. It is needless to enter into the details of soil formation beyond the general statement that clay is derived from the silicates of eruptive rocks, while sand is formed from the silica of quartz. The former due to a chemical decomposition, the latter rather to a mechanical subdivision. These two extremes have the following general composition as regards fertilizer constituents.

	Clay Soil, Per cent.	Sandy Soil, Per cent.
Potash	1.20	0.17
Phosphoric acid	0.15	0.11
Silica	72.52	81.01
Alumina	9.70	2.01
Lime	2.53	0.42

The presence of vegetable matter mixed with the soil gives that composition known as loamy. This vegetable matter is largely humus, a material of undetermined composition, and the function of which is still a subject of contention. The gradation of soils from heavy clay to sand is chiefly marked, by the varying proportions of clay and sand.

Using the given classification, the variation of the two leading principles is approximately as follows:

	Clay, Per Cent.	Sand, Per Cent.
Heavy clay	90	10
Medium clay	75	20
Loamy clay	65	35
Clay loam	55	45
Loam	40	60
Sandy loam	25	75
Loamy sand	15	85
Sand	5	95

Properties of Soils. Before considering a specific fertilizer, the agricultural value of these different soils must be reviewed. The general characteristics of a clay soil are fine texture and cohesion of the particles. It absorbs moisture from the air and draws it from the lower soil by capillary attraction, and retains water obstinately. If worked while wet it becomes hard and intractable. A sandy soil has little adhesion of particles, attracts little or no moisture from the air, and allows water to percolate through it readily, thus causing loss of fertilizing elements by leaching. It absorbs and retains heat well and is dry and warm, easily worked and will not bake. Its power of drawing moisture from below is about two-thirds that of clay. Soils intermediate between sand and clay take, in a modified way, the main features of both.

For purposes of agriculture the circulation of moisture in the soil and the temperature are of greatest importance. A soil having clay as its predominant constituent holds its water almost stationary, and when subjected to evaporation, through heat or drying winds, bakes badly. The soil water contains fine particles of clay in suspension and these are drawn to the surface and deposited by the evaporation of the water, thus forming an upper layer no longer porous. Evaporation ceases. The soil moisture, only a few inches below the surface, remains quiescent, and the closely packed upper layer also excludes heat and gases, the soil becomes cold, and those chemical processes necessary for the preparation of plant food in an assimilable form cease.

The best known remedy is applications of lime which throw down the suspended clay in the form of small granules, thus opening the pores of the soil and enabling a free circulation of water and the admission and action of gases and sunlight. With sandy soils evaporation does not bake and the movement of the soil waters is accelerated, but there is danger of exhausting the supply as the power of capillary attraction in this case does not greatly exceed a depth of 20 inches. These soils give free play to the action of gases and sunlight and maintain a temperature favorable to vegetation. Excessive evaporation is

prevented by thorough tilling; a surface layer of finely pulverized earth a few inches deep arrests evaporation while it still maintains a fair degree of soil porosity and consequently the admission of gases and sunlight is not retarded. The action of chemical fertilizer is more prompt with sandy than with clay soils. Sandy soils however must be kept at work so to speak. They lose fertilizer elements rapidly through leaching if not protected by vegetation. As to temperature, a dark-colored soil, other conditions being equal, is usually warmer than one of lighter color; a soil having its percentage of sand high will rise in temperature slowly but will retain the heat longer than either loam or a clay soil; a wet (clay) soil is uniformly a cold soil.

Function of Soil Moisture. Evaporation of soil moisture cools the soil as the heat necessary to vaporize the water is drawn from the land. Evaporation, however, draws the moisture from below for very considerable depths and the fertilizing matters suspended or in solution are brought by this process within reach of the roots. To quote from the Wisconsin experiments: "Soil water is constantly in motion. When rain falls the moisture sinks into the soil carrying along with it oxygen, carbonic acid, nitric acid, ammonia, etc., and rendering plant food available, a part of which may be lost in the drainage if the rainfall is excessive. When the rainfall ceases evaporation commences and the soil water begins to rise carrying along with it dissolved plant food which accumulates in the surface soil. This power which soils have of drawing up water from their lower depths is known as capillary attraction and may extend down 6 or 7 feet."

Some idea of the immense amount of soil water thus brought to the surface may be gained from the fact that with the average soil, clay loam under cultivation, 660 lbs. of water per square foot is evaporated yearly, that is, 28,750,000 lbs. per acre. Computing from the average analysis of soil waters, this quantity of evaporation would bring to the surface soil about 14 lbs. of ammonia and 57 lbs. of potash; the phosphoric acid does not appreciably enter into soil solution.

It must be understood that these fertilizing elements are not gained, they keep constantly in circulation; at night they sink only to rise again when the evaporation commences with the succeeding sunrise. By this circulating system the fertilizing elements are brought within reach of the plant roots and are utilized; were it suspended, the application of manures would have to be increased many fold, as the quantity of the nutrients in the immediate vicinity of the plant itself would have to supply all its requirements; and as the roots of a plant in ordinary farming practice occupy probably less than 5 per cent of the total space, it follows that the efficiency of one ton of fertilizer, as at present, would require an application of 20 tons to accomplish the same results with suspended circulation of soil waters. This is why commercial fertilizers contain a disproportionate quantity of phosphoric acid as

compared with potash and ammonia; the phosphates, to a great extent, take immediately in the soil an insoluble form and are rendered available as plant food only by the actual contact of the plant root hairs.

Action of Carbonic Acid on Soils and Rocks. All fertile soils contain a considerable amount of organic matter, and the presence of oxygen is necessary to accomplish its decomposition. Soils also contain innumerable bacteria, a part of which at least, are intimately concerned in the decay of organic matter and cannot live without oxygen.

One class of these bacteria decompose part of the soil's organic matter with the formation of carbonic acid gas. Water dissolves its own volume of carbonic acid gas under ordinary pressure, forming a solution of carbonic acid, $CO_2+H_2O=H_2CO_3$. With increased pressure a much greater amount is dissolved. When water is so charged it has a high solvent power for the carbonates of lime and magnesia, protoxide of iron and manganese. These salts are nearly insoluble in pure water. In this way carbonic acid plays a part of great importance in the growth of plants, since it enables water to convey to plants many fertilizing substances which are otherwise hardly available.

It is interesting to note here that the leaves of plants are white, in the absence of iron, and not green. By means of the microscope, the chlorophyl grains have been seen to grow and continue to prosper, as soon as a little iron was furnished to plants that had previously been without it.

Humus. Humus is a generic term applied to a group of closely allied substances, which collectively form the organic matter of soil. It cannot be said that the precise chemical composition of humus is known, though a great deal of labor has been devoted by chemists to the study of the compounds, and several tolerably well defined chemical constituents are thought to have been isolated. The more clearly understood of these constituents are ulmin and ulmic acid, humin and humic acid, crenic acid, and apocrenic acid. Among the less known, the action of which is not yet understood, are xylic acid, saccharic acid and glucinic acid, besides a brown humus acid containing carbon, 65.8 per cent; hydrogen, 6.25 per cent; and a black humus acid containing carbon, 71.5 per cent; hydrogen, 5.8 per cent.

According to Mulder, the principal humus compounds are composed of carbon, hydrogen, and oxygen, in proportions as given in the following table:

ULMIN AND ULMIC ACID

Carbon......67.10 per cent, corresponding to $C_{40}H_{28}O_{12}-H_2O$
Hydrogen.... 4.20
Oxygen......28.7

HUMIN AND HUMIC ACID

Carbon......64.4 per cent, corresponding to $C_{40}H_{24}O_{12}-3H_2O$
Hydrogen.... 4.30
Oxygen......31.30

APOCRENIC ACID

Carbon......56.47 per cent, corresponding to $C_{24}H_{24}O_{12}-H_2O$
Hydrogen.... 2.75
Oxygen......40.78

CRENIC ACID

Carbon......45.70 per cent, corresponding to $C_{24}H_{24}O_{12}-3H_2O$
Hydrogen.... 4.80
Oxygen......49.50

Materials Furnishing Nitrogen; Guano. On the coast of Peru, lie the Chincha Islands. These islands and the mainland opposite are in the dry zone of Peru in which rain seldom falls. They are small, high and rocky, barren and uninviting; yet from them has come vast wealth. Guano to the value of one thousand million dollars has been taken from the Chincha Islands. It is doubtful if there be another spot of equal size on the earth which has yielded so much wealth as these guano beds. These islands, however, are not the only source of Peruvian guano, as the Macabi, Guanape, the Lobos, Ballestas, and the Huanillos, as well as scores of small islands have also furnished large quantities.

The word guano is the Spanish rendering of the Peruvian word *huanu,* meaning excrement. There are many varieties of Peruvian guano having different fertilizing values due to their different chemical constituents, but they all are alike in their origin. Guano is mainly the excrement of marine birds mixed with the remains of the birds themselves and the fish they have brought to land. In some cases on the Chincha Islands the deposits are from 160 to 180 ft. thick. The lower strata of such deposits may be thousands of years old.

Nowhere else in the world are marine birds found in such vast quantities as along the west coast of South America from Panama south to Chile. The larger number of these birds have their roosts and breeding places on the Peruvian Islands, or on points of the mainland. Their presence in such vast numbers is due to the quantity of fish found along these coasts.

Cormorants, pelicans, sea gulls, marine crows, in flocks numbering hundreds of thousands may be seen in these regions, while the rainless climate preserves the guano deposited. There are hundreds of bird islands in other parts of the world but the excrement and remains of birds found thereon are not the same as Peruvian guano, although the deposits may possess value for fertilizing purposes. Even with the Peruvian guano, analysis shows great differences.

All excrements contain nitrogen in the form of urates and salts of ammonia, but these are to a large extent lost unless the manure is at once applied to the land and even then the nitrogen may be washed out before it can become available for the plant. When left exposed to a humid atmosphere or when rain is allowed to fall on it the nitrogen salts are quickly leached out. The Peruvian guano, in its natural state, never having been exposed to rain or dampness, has retained its nitrog-

enous properties and as it is rich in all three elements of plant food it is more valuable than other guanos.

Guano has been used in Peru for centuries. As early as 1806 it was used in England, and in 1824, fifty vessels loaded annually at Chincha. It was used in the United States as early as 1832. Baron Humboldt in 1804 was the first to make the article known to Europeans, its commercial importance there dating from 1844. As before stated, the Chincha Islands were the first exploited. Nine million tons were extracted in ten years. Other deposits were developed in 1870. The Ballesta, Macabi, and Guanape Islands yielded 1,500,000 tons. Next the Lobos Islands were worked as well as the enormous deposits of the Province of Tarapaca on the south coast of Peru.

In reviewing this subject, L'Engrais of Paris estimates that in forty years over 18,500,000 tons were taken from these localities or about 440,000 tons annually.

As the penguins and pelicans are very voracious each bird is capable of furnishing on an average, about 32 gms. of excrement per night. It is estimated that 100 kgms. of guano, containing 14 per cent of nitrogen and 10 per cent of phosphoric acid, require the consumption of 600 kgms. of fish containing 2.3 per cent nitrogen and 1.7 per cent phosphoric acid. An annual deposit of 40,000 tons is, therefore, the digestive product of 3,420,000 pelicans. It is reported that while the old beds have been considerably reduced there are layers 30 ft. thick which have not been touched and which are still forming.

The Caribbean deposits are much lower in nitrogen than the Peruvian, but they run very high in phosphoric acid. In these much of the nitrogen has been leached out by the action of rain. The deposits found on the islands of Sombrero, Navassa, Aruba, Curacoa, Orchillas, Roncador, and the Pedro and Morant keys are similar to those found on the Caribbean coast.

The following table shows analyses made by the author on various grades and kinds of guano:

	Ammonia.	Phosphoric Acid.	Bone Phosphate.
Navassa (first cargo, 1856)	None	31.75	69.31
Brazilian	None	27.82	60.73
White Mexican (1858)	None	25.88	56.60
Peruvian standard	10.20	12.14	26.50
Peruvian (Lobos)	5.60	14.95	32.64
Peruvian (Chincha)	12.70	17.80	38.85
Grand Caymans Islands	None	25.16	54.92
Mona Island	None	24.21	52.85
Aves Island	None	18.92	41.30
Cay Verde (light)	0.80	29.85	65.16
Cay Verde (dark)	0.50	29.90	65.27
Orchilla Islands (soft)	None	20.60	44.97
Booby Island	1.30	10.54	23.00
Oruba	None	34.65	75.64
Avalo	None	30.50	66.58

The guano is taken out by shovel and pick. As the coasts are rough and few harbors exist, loading of steamers can be done in calm weather only. The water is very deep and large steamers can anchor close to the shore so that most of the guano can be loaded directly into the steamer from the shore by means of cable trams. In some cases, it has to be taken to the steamer in boats.

Calcium Cyanimid. This is a product derived by heating calcium carbide in an atmosphere of nitrogen. The reactions are intricate, but may be represented by the following equation: $CaC_2+N_2=CaCN_2+C$. The technical procedure is simple, but care must be taken in carrying out the details. The nitrogen must be technically pure and the complete nitrification of the carbide, necessary to produce a high grade product, is dependent upon progressive and cumulative reactions, which once started may not be checked or diverted at any stage except at the cost of the quality of the final product.

The following is a typical raw cyanimid proximate:

Calcium carbide	0.51%
Calcium cyanimid	68.02
Calcium carbonate	0.35
Calcium oxide	12.39
Free carbon	13.79
Silicon carbide	1.17
Aluminum carbide	1.67
Iron carbide	1.53
Not determined	0.57
Total nitrogen	23.81%
Total calcium as CaO	60.65

When freshly made cyanimid is a rich black crystalline substance Upon exposure to moist air the calcium oxide present hydrates, not only adding weight to the material, but also increasing its volume. It was at first stated that a loss of nitrogen occurred but this is not true. While the characteristic odor of ammonia is noted, careful check tests taken at various times have failed to show appreciable loss of nitrogen. For commercial uses, this hydration of the free lime accompanied by increase in volume is undesirable.

Small quantities of carbides, phosphides, and sulphides are frequently present in raw cyanimid, which are undesirable for many of the uses of cyanimide and notably so for its use as a fertilizer. When applied to the soil these materials form, after decomposition, acetylene, phosphine, and sulphuretted hydrogen. All of these gases are distinctly poisonous to vegetation and particularly so to seedlets at or during the period of germination. When cyanimid was first distributed to experimental agriculturists, it frequently contained as much as 8 to 10 per cent of these substances. Consequently the records of experimental research

show many instances of poisonous action which were naturally charged against the cyanimid itself.

To prepare adequately the raw cyanimid for incorporation into fertilizers several processes have been developed and much costly machinery designed. The object of such processes being simply to hydrate all the caustic lime and to dislodge and expel as a gas all the substances in the raw cyanimid which will produce acetylene, phosphine, and hydrogen sulphide.

The finished product sold under the name of Improved Cyanimid has the following composition. (This product is complementary to the analysis of the raw cyanimid given above.)

Calcium cyanimid	29.26%
Calcium carbonat	0.21
Calcium nitrate	20.06
Calcium hydrate	28.78
Sodium cyanimid	10.38
Free carbon	7.89
Silica	1.03
Alumina	1.37
Ferric oxide	0.69
Not determined	0.33

Total nitrogen	17.01%
Total calcium (CaO)	34.73
Nitrate nitrogen	3.39
Cyanimid nitrogen	13.62

Some 20 per cent of the total ammonia in improved cyanimid is present as nitrate, the remaining 80 per cent being present as cyanimide.

The combined nitrogen of cyanimid does not exist as ammonia in the material as marketed, but as an amide. Thus instead of being combined with three hydrogen atoms it is joined to two. In the presence of acids or of water cyanimid nitrogen slowly changes to the ammonia form.

For comparison the following two equations are given as being typical of the change in ammonium sulphate and calcium cyanimid due to action of the soil:

$$(NH_4)_2SO_4+Ca(OH)_2=CaSO_4+2H_2O+2NH_3$$
$$CaCN_2+3H_2O=CaCO_3+2NH_3$$

These two reactions may be effected by acid or basic salts. The results are the same, however, and the final product by the action of simple soil agencies in both cases is ammonia. Consequently, as a fertilizer, cyanimid nitrogen must be classed as ammonia nitrogen. It is true that cyanimid may pass into solution in an acid soil as urea, thus:

$$CaCN_2+2H_2O=CaO+CO(NH_2)_2.$$

Urea, however, in dilute solutions, slowly changes to ammonia (unless combined with a strong acid), as follows:

$$CO(NH_2)_2+H_2O=CO_2+2NH_3.$$

The soil contains far more water than lime, in the form of a soluble compound, and lime must be in solution to displace ammonia from sulphate of ammonia. Under ordinary soil conditions cyanimid nitrogen is quite as rapidly converted into ammoniacal solutions as is sulphate of ammonia.

Calcium cyanimid is moderately soluble in cold water or water at ordinary soil temperatures. Its availability as a fertilizer as technically determined, is about the same as that of sulphate of ammonia and much greater than that of dried blood. It is doubtful, however, if in its actual crop-making power, in an average of all soils and under all conditions, it is more valuable than dried blood, or less valuable than ammonium sulphate. Under working soil conditions, in actual crop-making operations, relative availability is probably of less moment than intelligent application and thorough husbandry.

The latest technical observation upon the use of cyanimid in agriculture is the report of Prof. Jacometti of the Agricultural Academy, Turin, Italy, as follows: "Both calcium cyanimid and Norge nitrate have a fertilizing value about equal to that of sulphate of ammonia and nitrate of soda."

The following table is given as showing the relative fertilizing worth of different forms of ammonia in production of sugar cane.

Cane.	Sugar Made, Relative Tons.	Ammonia, Cost per Ton of Sugar.	Ammonia, Worth per Unit.
Cyanimid	1.00	$2.61	$2.65
Nitrate of soda	0.73	3.22	1.94
Sulphate of ammonia	0.66	3.41	1.75
Tankage	0.73	3.93	1.93

Dry Fish Scrap. The menhaden (*Brevoortia tyrannus*) belongs to the family Clupeidæ and has many local names. On the Maine coast it is called pogy, bony fish, moss-bunker; in Massachusetts, hardhead bunker; in Delaware, bug fish, in addition to those already given; on the Virginia coast, old wife, cheboy, ellfish, bug fish, green tail, and bughead; in North Carolina, fat-back and yellow-tail shad.

When full-grown the fish weighs from 10 ounces to 1½ lbs. and measures from 12 to 15 ins. in length. They are found in immense schools on the American North Atlantic coast from the Bay of Fundy to the Mosquito Inlet, Florida. Its usual habitat is the bays and rivers, some-

[1] From an article prepared for the *American Fertilizer* in the office of the Technologist of the American Cyanimid Co.

FIG. 210.—Screw Press. American Process Co., New York.

FIG. 211.—Cooker. American Process Co., New York.

FIG. 212.—Direct Heat Dryer. American Process Co., New York.

times as far as the brackish water extends, and ocean-ward as far as to the Gulf Stream. On the approach of warm weather the schools begin to appear and remain until cold weather. Approximately a temperature from 60 to 70° F. appears favorable. In the Chesapeake Bay the season extends from March and April to November and December. The New Jersey fishing season begins about May 1st and ends about the middle of November. The habit of the fish is to congregate in very large schools and then swim along close to the surface of the water, packed closely side by side and tier on tier. As many as 450,000 tons of these fish have been taken in a single season.

As soon as the fish appear, steam and sailing vessels start out from the numerous factories along the coast and remain in commission until the fish have disappeared in the fall. In the spring the northern factories send their steamers south and they follow the fish north. In the fall they follow them south again until they get beyond the point where it is economical to fish for them. The average steamers are of about 80 tons burden and usually about 90 ft. long; such a vessel will take a cargo of from 250,000 to 300,000 fish. The crew consists of about 17 men. Larger steamers are used by some of the factories and in such cases two seines are carried. These steamers will hold from 900,000 to 1,200,000 fish and have crews of 24 men.

When a school of fish is sighted, the steamer gets as close as possible without scaring the fish and then lowers the two seine boats of whale boat pattern. The seine is a net from 750 to 1800 ft. long and 75 to 150 ft. deep with the usual fitting of cork and sinkers, and so arranged that the bottom may be drawn together, thus making a purse in which the fish are held. The two boats, each carrying an equal amount of the net, start in opposite directions around the school and when they have met, start pulling in the purse string. When the bottom is closed the steamer comes up and the fish are scooped from the net by means of large scoops worked by a derrick on the steamer.

When a steamer has a load it returns to the factory, as the fish, if kept too long, soon turn soft and are then very difficult to handle.

On reaching the factory, the fish are unloaded by being shoveled into a traveling conveyor which takes them to a belt which carries them into the store shed. From here they are carried to a continuous steam cooker, Fig. 211, where the oil cells are broken and the fish bodies broken up. This requires but a few minutes, when the fish are run into screw presses Fig. 210. On leaving the cookers they contain about 75 per cent of water. The screw presses can press the fish down to about 45 to 50 per cent of water. Most of the oil is here liberated.

The water and oil are run into large settling tanks and the oil which rises to the top is taken off.

The fish from the presses then go to direct-heat or steam heated cylindrical dryers, Fig. 212. They are dropped into the hot end of the dryer

where the flame from either soft coal or oil is pouring in. The water in the scrap prevents the burning of the fish as it immediately takes up the heat. The scrap falls to the bottom of the dryer and is carried around as it revolves and showered down through the hot gases. On reaching the end of the dryer it is cool enough to handle and contains about 8 per cent water. It is now picked up by a traveling belt and run to the storehouse where it is bagged ready for shipment. Great care must be taken in the storeroom, on account of the combustible nature of this material, owing to the presence of the oil left in it. It heats very rapidly if left in large piles and must be cooled by turning over.

The capacity of a factory is usually calculated as the number of barrels per day of fish that it can handle. One barrel contains 300 fish. A large and well equipped factory will handle 700 barrels of fish per hour, turning same out as wet acid scrap, or if the dryer capacity is equal to the cooking and pressing capacity as dry scrap.

To produce one ton of dry scrap requires an average of 50 barrels of fish, while to make one ton of acid scrap (wet) requires 30 barrels of fish. In a good season about 3 gallons of oil per barrel of fish is recovered.

Wet Acid Scrap. Where the plant does not have enough dryer capacity to take care of the catch, the excess is made into wet acid scrap. The fish scrap from the presses is acidulated with from 60 to 80 lbs. 60° Bé. sulphuric acid to the ton of wet scrap. This converts some of the bone phosphate into the available form and at the same time preserves the scrap from decomposition. Good acid scrap that has not lain long in piles will analyze on 50 per cent water basis as high as 7.50 to 7.75 per cent ammonia.

In many small factories instead of screw presses, hydraulic presses are used and the wet scrap is dried in the open air on large wooden drying floors.

The scrap must be turned over frequently and this is done by the use of harrows drawn by a horse. It has then to be piled, left to heat to some extent, again spread and turned. If the scrap is wet by a storm, the process has to be repeated. Dry scrap will run about 10 per cent water and 10.50 to 11.50 per cent ammonia, and will still carry 8 to 12 per cent oil.

Bat Guano. Deposits of this material are not of very great extent, consequently its importance as a fertilizer is small. It is used in localities where it is found. It is of very variable composition and by many is not considered of much value. The price paid for the ammonia content is not on a par with other sources of ammonia.

Horn and Hoof Meal. The horn and hoofs not available for more valuable purposes are slightly cooked until they become friable and are then ground to a fine powder for use. They run from 4 to 6 per cent water and 15 to 17 per cent ammonia.

Hair Stock. Most long hair is used for other purposes than fertilizers, but large numbers of South American hides are imported for making leather and the short hair from these hides after being removed by the sweating process in tanneries is utilized as a source of ammonia for fertilizer manufacture. The ammonia of the hair without treatment is not available for plant food, but during the process of making acid phosphate the hair is subjected to the hydrofluoric acid fumes given off when the phosphate rock is treated with sulphuric acid and becomes decomposed; the sulphuric acid then unites with it and forms ammonium sulphate, thus furnishing available ammonia.

Leather Scrap. This is treated the same as hair stock in most cases, though in some cases it is dried till it is brittle and then ground into "leather meal."

Many states have laws against the use of either hair or leather as fertilizers.

Cotton-seed Meal. The products obtained from the cotton seed are lint, oil, hulls, and meal. The meal only is used in the manufacture of fertilizers.

Cotton-seed meal is obtained by grinding the cake which is left when the oil is pressed out. Its chief uses are as a cattle food and as fertilizer. The meal damaged by over heating can be used only for fertilizer purposes.

The average amount of meal, hulls, lint, and oil per ton of seed is as follows:

Meal	713 lbs.
Oil	282 "
Lint	30 "
Hulls	975 "

Fertilizing Value of Cotton-seed Meal. The plant food in cotton-seed meal is chiefly nitrogen, so that its fertilizing value depends upon the quantity of nitrogen present. It contains, however, an appreciable amount of phosphoric acid and potash. The average of 204 analyses is as follows:

Nitrogen	6.79%
Phosphoric acid	2.88
Potash	1.77

The trade value for these constituents is variable but taken at, nitrogen, 13 cents, phosphoric acid, 7 cents and potash 6 cents, the value as per above analysis per ton would be:

Nitrogen	$17.65
Phosphoric acid	4.03
Potash	2.12

This gives a total value of $23.80 per ton of 2000 lbs.

In using cotton-seed meal as a fertilizer it must be borne in mind that it is essentially a nitrogen provider, hence if the soil requires phosphoric acid and potash as well as nitrogen, the meal should only be used in connection with some form of fertilizer furnishing these other materials.

While the hulls are not used as fertilizer, still it is of interest to note their analyses as follows:

Nitrogen	0.69%
Phosphoric acid	0.25
Potash	1.02

Taking same values as above this would give a value of $3.35 per ton.

In 1905, 3,308,930 tons of cotton seed were produced with a value of $51,309,175.

Other Meals Not Much Used. Castor pomace obtained after oil pressed from castor beans, grape or tartar pomace, the refuse argols from manufacture of cream of tartar, and flaxseed meal obtained from pressed flaxseed are not of much importance. They contain varying amounts of nitrogen, phosphoric acid, and potash.

Utilization of Tank Water and Press Water from Tankage. After meat scrap has been cooked in the rendering tanks, it is allowed to settle to the bottom. The water and grease rise to the top and the grease is drawn off. The tank water is then run into a storage vat together with the water pressed from the tankage. This storage tank is provided with heating coils in the bottom. The water is here heated to about 170° Fahr., at which temperature any further grease which rises is skimmed off. It is important to remove as much of the grease as possible as it will interfere with the further process of evaporation. Most of the evaporating is done in double and triple effect evaporators. Fig. 213. Working with a triple effect the tank water is drawn into the first effect in such a quantity that it covers the heating space. When the steam is turned on it brings the water into rapid circulation and it begins to throw off vapor, which is conducted into the tube space of the next effect. When the first effect is working under a vacuum of 5 to 10 ins. and under a steam pressure of about 2 to 5 lbs., the second effect boils under a vacuum of about 15 ins. The vapor which then arises from the second effect is conducted into the tube space of the third effect which boils under a vacuum of 26 ins. The vacuum pump attached to the evaporating plant is sucking directly on the third effect and condenses the vapor which is thrown off from this third effect.

The tank water is kept at the same level in all three effects and as it boils down it is drawn over from the second to the third and from the first to the second, and fresh water is run into the first effect. In some evaporators this feeding of the tank water is automatic, the valves being left open so as to allow the tank water to run slowly from one effect

to the next until the liquid in the third effect is so heavy that it is ready to be pumped out.

The density of this tank water (which after completion of evaporation is called " stick ") is from 26 to 30° Bé. at the temperature of the evaporator. This " stick " is pumped up in a storage vat provided with agitators and from this vat it is either run to the dryers which are drying the tankage and thus mixed with it, or is mixed with chemicals such as green vitriol and dried on internally steam heated rotating drum dryers. In this latter condition after being dried it is called " concentrated tankage " and runs 15 to 17 per cent ammonia. The green vitriol is added to keep the material from absorbing moisture and reverting back to the sticky condition, as it is very hydroscopic. In present practice most of the " stick " is dried with the tankage, thus raising the percentage of ammonia in the tankage and doing away with the handling of a second product.

Fig. 213.—Evaporator. American By-Product Co., New York.

Slaughter House Tankage. In all slaughter houses the scrap meat is saved and treated for the production of "tankage." As all this material has more or less grease still adhering to it, it is first placed in large tanks and boiled under pressure till the grease has left the meat and the bone. The scrap is then allowed to drop to the bottom of the tank and the liquor is drawn off into large vats. After the grease has risen to the top it is withdrawn. The remaining liquor is then treated for its fertilizing constituents as given elsewhere under " concentrated tankage."

The scrap meat and bone, or as it is called "tankage" is now pressed to free it as much as possible from the water and adhering grease and is then dried in rotary direct-heat or steam dryers. It is then ready for sale.

In plants where the liquors are evaporated for "concentrated tankage" it is a general practice to mix the "stick" or thick liquor obtained by evaporation directly with the tankage before drying. This raises the percentage of ammonia and at the same time does away with the making of a second product.

There are several grades of tankage made, depending on the quantity of bone present. In small plants practically all the bone, except the very largest pieces, are left with the tankage. This gives a product running low in ammonia and high in bone phosphate. Such tankage may run from 5 to 8 per cent ammonia and up to 25 to 30 per cent bone phosphate.

In the larger plants, such as the Chicago packing plants, more care is taken to remove the bone, thus giving a tankage of higher ammonia content and lower bone phosphate. This will run about 11 per cent ammonia and 15 per cent bone phosphate.

There are three usual grades of tankage quoted in daily market reports as follows:

11 per cent ammonia and 15 per cent bone phosphate,
10 per cent ammonia and 20 per cent bone phosphate, and
9 per cent ammonia and 20 per cent bone phosphate.

The steaming, pressing, and drying do not remove all the grease. The best that can be done is to get it down to 6 to 8 per cent on the basis of the dried material, while frequently where factory practice is bad it will run as high as 20 per cent. This, of course, lowers the percentage of both ammonia and bone phosphate. As the grease balls the material and renders it hard to grind, its presence in large quantity leaves the tankage in bad condition for making into complete fertilizer. Where the fire hazard is not too great, and the plant is large enough, naphtha extraction is used to remove this grease from the dried tankage. Frequently in neighborhoods where a centrally located plant can obtain tankage from a number of small packing houses, naphtha extraction is employed, so that the grease and the grease-free tankage may be obtained. The grease is removed in these plants by subjecting the tankage to the solvent action of naphtha under pressure in large tanks holding from 10 to 20 tons of tankage. After a number of hours treatment, the temperature is reduced and the naphtha withdrawn. Live steam is then blown in to remove the excess of naphtha, the tankage finally withdrawn and spread over a large area to let the remaining naphtha evaporate. This process will remove all but 1 or 2 per cent grease.

Garbage Reduction.[1] The garbage is collected in wagons which have watertight steel bodies and sectional canvas covers. It is hauled to the central loading station and dumped into the garbage cars. The cars are constructed in semicircular bodies designed especially for handling garbage.

[1] Article by I. S. Osborn, engineer in charge of design and construction, Columbus, Ohio. Taken from *The American Fertilizer.*

The garbage when delivered is weighed on railway track scales and then run into the green garbage building, Fig. 214, on a siding which extends through it. The free water is drained off through a gutter extending the full length of the building. The swill water from the gutter is drained into a catch-basin, from which it is discharged into the grease separating tanks after which it is evaporated.

FIG. 214.—Garbage Reduction Plant.

The garbage is sorted and shoveled into a scraper conveyor, extending the full length of the building. This is a Jeffrey type conveyor and extends to the main building, carrying the garbage along the incline truss to the top of the main building and then along the bottom chord of the roof trusses and over the tops of the digesters. Connecting the conveyor with the digesters are swivel spouts which discharge the garbage directly into the digesters.

The digesters are 7 ft. in diameter by 14 ft. in length and have a capacity of 10 to 12 tons each. The inside is lined with cement and tile 1½ ins. thick so as to protect the digester from wear, due to the agitating of the gritty matter when boiling, and at the same time to resist the action of the acids which would attack the metal. The digesters are arranged in nests of four and are connected with a common receiving hopper which is directly connected to the roller presses. The four digesters, one receiving hopper and a roller press are called one unit. The time required for cooking varies with the kind of garbage, but averages 6 hours with steam at 60 to 70 lbs. pressure as it enters the digesters.

The presses which are connected with the hopper are of the continuous roller type, especially designed by Charles Edgerton for handling garbage. They are directly connected to the bottom of the receiving hopper so that the material from the digesters passes through the presses without being exposed. The press is provided with an upper and lower conveying apron. The upper apron is made of ½-in. steel slats riveted

to a heavy forged steel chain. The upper apron acts as the bottom of the receiving hopper, and when the press is running, carries the material through the feeding rolls and discharges it onto the lower apron. The lower apron is made of perforated slats $\frac{3}{8}$ in. in thickness and passes between six cast iron rolls arranged in pairs.

The pressed material is discharged at the front of the press into a Jeffrey scraper conveyor, which carries the material to the second floor of the drying department. The water and grease flow from the presses to catch-basins in the grease separating room. The grease is drawn off and pumped into storage tanks ready for shipment.

The liquor coming from the presses carries more or less solid matter in suspension. These solids are known as muck and silt. The muck settles to the bottom of the grease separating tanks and the silt rises to the top of the water. The tank water, after the grease has been separated, is drawn off to a large storage tank outside the building. The tank water contains 5 to 7 per cent of solids in solution; it is concentrated in a triple effect evaporator. After concentration the tank water is drawn off by a Magma pump and discharged into a storage tank on the second floor.

The muck and silt from the grease separating tanks are placed in a screw press from which the liquor flows to the catch-basins and the solids pass along the scraper conveyor to the dryer room. The solids are then fed to a revolving steam heated cylindrical dryer. The material is fed into the dryer continuously and discharged by means of two short spiral conveyors placed at the opposite end.

The dried material is then passed through the revolving screen. The screened tankage is then placed in the vacuum or mixing dryers, and the concentrated syrup added. The dry fibrous material acts as a filler and enables the moisture in the syrup to be driven off. The addition of the syrup to the fibrous material produces a higher grade of tankage from a mechanical and fertilizing standpoint.

The dryers are 15 ft. long and 5 ft. in diameter. Through the center of each dryer is a shaft to which paddles are attached for agitating and mixing the material. When dry, the material is discharged into another spiral conveyor connected to a Jeffrey bucket elevator, which discharges the tankage onto the third floor, where it is stored until shipped.

The Phosphate Rock Industry. From time to time various deposits of phosphate rock have been found and mined throughout the world, but the principal workings to-day are to be found in Florida, South Carolina, and Tennessee in the United States, in Algeria and Gafsa in North Africa, and in Ocean and Christmas islands in the far east.

The first serious attempt to obtain phosphate in this country was in Canada, mining what is known as Canadian apatite. This is a very high grade material, but it was very expensive to mine and when in 1870

the South Carolina, and in 1888 the Florida deposits were marketed, it could not compete with them. The rock in South Carolina is found in two grades—river and land pebble. It is deposited in considerable quantities along the margins of navigable streams and in the river beds between Charleston and Beaufort. The rock of Northern Africa, on account of its locality, is consumed entirely in Europe, and the production of the East Indies finds its market in Japan and Australia as well as in Europe.

Florida Phosphate. In 1889 pebble phosphate was discovered in De Soto County. Several months later land rock phosphate was uncovered at Dunellon in Marion County. This is the most valuable of the Florida phosphates and its discovery at once caused the investment of large amounts of capital. In the following year plate rock phosphate was discovered at Anthony in Marion County. Land rock phosphate is unlike the river and land pebble phosphate. The deposits in Florida are as a rule about 175 by 15 miles in area, parallel with the coast, and about 20 miles inland. Plate rock phosphate is mined only in a limited section of Marion County. It acts as a covering for limestone cones and is from 6 ins. to 1 ft. in thickness.

Pebble rock phosphate is almost entirely of marine formation and is located in the beds of small rivers and lakes and in areas originally covered with water. It is found far back from the coast in areas about 20 by 60 miles in extent and in tonnage produced surpasses both land and plate rock. Pebble rock occurs in the form of rounded pebbles varying up to a size somewhat smaller than a hen's egg. When a deposit is located it is first thoroughly prospected by boring with a core boring machine, as by this means the depth of the bed is ascertained as well as the grade of the various layers of phosphate encountered.

The mining is hydraulic. Powerful streams of water are thrown against the edge of the bed and the phosphate gravel together with the sand and clay is washed into a hole about 10 ft. in diameter and 10 to 15 ft. deep. The gravel is sucked up from this hole by means of a pipe and run to the mill which may be half a mile or more away. Here it is passed over screens which allow the fine silt and sand to escape while the phosphate pebbles are caught. This serves to wash the rock and it is then passed through direct-heat rotary dryers and carried by belts to the storage bins, ready for shipment.

As contracts are made for from 3 to 10 years shipments, it is very necessary that the property shall be thoroughly prospected, as it is necessary to know what grade rock can be obtained from different parts of the property. The prospecting is remarkably accurate. The actual factory returns usually show a yield agreeing within 1 per cent of what the prospecting had indicated.

Another method of mining this rock is by means of dredges which scoop the rock from the bottom of the river or lake and dump it into

cars which carry it to the mills. The extent of the bed of rock is ascertained by prospecting in a manner similar to the above until the area suitable for working is determined. The dredge is then brought up the river to the point where operations are to begin and starts digging into the side of the bank throwing the scooped up material into the cars. In some cases suction dredges are used and a partial separation of the rock and clay made on the dredge, the rock being dumped into cars and the sludge thrown out.

The bulk of the land pebble runs from 68 to 70 per cent *bone* phosphate, while high grade hard rock runs 76 to 78 per cent. The iron and alumina content is about 2 to 3 per cent.

Tennessee Brown Rock Phosphate. The Tennessee phosphates occur almost entirely in silurian and devonian starata, but more particularly in the former, and in the transition strata between the two. In December, 1893, blue rock phosphate was discovered in Hickman County. The beds of brown rock in this vicinity which are the finest phosphate deposits in the world, were not worked till later. Some 45,000,000 tons of this brown rock are estimated as being available for mining in this district. New fields are being continually opened up, railroads built and large quantities shipped. As the brown rock of this locality is gradually used, the vast blue rock fields of Maury, Hickman, and Lewis Counties will come into active development.

This brown rock lies in strata formation with layers of clay and earth as overburden. This overburden is stripped by hand or steam shovel and the soft wet phosphate taken out either by hand or steam shovel. It is carried to the washers where it is freed from the most of the clay and dirt. On account of the porous nature of this rock, the clay is disseminated all through it and it is very difficult to get rid of all the clay by the use of simple log washers. Many types of washers are used, the most efficient being the form used in cleansing glass-makers sand. This is done by pumping the fine material through pipes having sharp angles where the pressure is greatly increased. The clay is washed out in this manner and the clean rock is finally delivered to very deep settling tanks where the muddy water holding the clay in suspension is drawn off and the heavier rock which settles, after the tank is filled, is dried in rotary direct-heat dryers and is then ready for shipment.

This method is so efficient that a hand-car load of rock dumped through a space of 20 ft. will hardly raise any dust, whereas the rock cleaned by simpler and less effiicent means will carry so much clay dust that a cloud of dust rises whenever it is disturbed.

Many of the smaller plants simply sun-dry the material, after it is dug, by spreading it on the fields and frequently turning with a harrow. When the rock is kiln-dried, large piles of wood are prepared about 10 ft. across and 20 to 40 ft. long and 5 to 6 ft. high. The wet rock i

piled on top and the wood fired. In case a storm comes up during the drying the whole operation has to be repeated, causing considerable expense.

Much of the material that is washed in log-washers or by use of revolving screens is more thoroughly cleansed of the adhering clay by blowing a very strong blast of air through the direct-heat dryers thus blowing off the lighter dust, or floats. This gives a fairly good material but the loss in phosphate is rather large as the floats will test from 50 to 60 per cent *bone* phosphate. It is very important to reduce the clay as much as possible as well as the iron and alumina phosphate, as these prevent the making of high available acid phosphate.

Tennessee Blue Rock. This rock is found in a territory bounded approximately by a trapezoid having at its four corners Centreville in Hickman County, Kinderhook and Mt. Joy in Maury County, and Lewis Monument in Lewis County. Traversing this territory are Duck River, Indian, Swan, Blue Buck, and Cathay's Creeks, and outcropping along these valleys and underlying the ridges between them are deposits of blue rock running in *bone* phosphate from 60 to 78 per cent, with less than 3 per cent iron and alumina oxides, that will aggregate nearly 40,000,000 tons.

Tennessee White Rock Phosphate. The deposits of white phosphate in Perry County, Tenn. have been formed by the deposition of phosphate from solution on the beds of limestone caverns. They are not of very great extent. Most of it is mined by means of open cut work although some tunneling is done. It lies in beds varying from a few inches to several feet in thickness.

Carefully selected specimens of the lamellar variety have run from 85 to 90 per cent of *bone* phosphate. The less dense, greenish material contains some ferrous iron and runs slighlty less than 80 per cent.

South Carolina Phosphate Rock. This rock occurs in the form of nodules ranging in size from a pea to pieces the size of a man's head, and is found both upon the land and in the river beds. On the land the phosphate bearing strata are usually covered with sand to a depth of 6 to 10 ft., and vary from one to several feet in thickness. The mining on land is done by steam shovels which remove first the overburden and then the rock, which is screened, washed and dried. In the river beds a dredge is used to get out the rock which is then dried as usual. It runs from 50 to 60 per cent *bone* phosphate and about 6 per cent iron and alumina oxides.

The Western Deposits of Phosphate. As yet these deposits occurring in northern Utah, southeastern Idaho and southwestern Wyoming, while very large, are at present not developed, but they promise to be very large producers in the near future.

Phosphates in the South Seas. The islands of the Pacific Ocean contain the largest known deposits of high grade phosphates. The

deposits in Ocean and Pleasant Islands in the Gilbert group are estimated at 50,000,000 tons. About 300,000 tons yearly is being mined and shipped. About 100,000 tons is taken to Japan, 80,000 to Australia, and the remainder to Europe. Europe also receives yearly about 100,000 tons from Christmas Island. Recently good grade phosphate has been found on the islands in the French colony of Tahiti and dependencies. These islands, Makatea, Matahiva, and Niau, lie in the northwestern part of the Tuamotu Archipelago. The high grade deposits in Makatea are estimated at 10,000,000 tons with many million more tons of lower grade. These deposits range from 73 to 80 per cent *bone* phosphate content. It is estimated that when the works are completed and working at full capacity 200,000 tons yearly will be shipped. This island, together with the island of Angaur about 600 miles to the east of the Philippine island of Mindanao, is a coral island and has been for ages the resort of countless flocks of marine birds. Their excrement accumulated in vast quantities, but was not preserved unchanged as is the case in the guano islands. The heavy rains of this section of the Pacific caused a steady leaching of the soluble phosphates, which, coming in contact with the porous coral growth beneath of pure calcium carbonate gradually changed it into calcium phosphate.

Thomas or Belgian Slag. Thomas or basic slag is a by-product in the modern method of steel manufacture from ores containing noticeable quantities of phosphorus. The process of removing the phosphorus from the ore was first discovered by the English engineeers Gilchrist and Thomas and consists in adding to the converter containing the milled ore a definite quantity of freshly burnt lime, which, after powerful reaction, is found to be united with the phosphorus and swims on the top of the molten steel in the form of a slag.

The composition varies according to the character of the ore and the success of the process for removing the impurities. The following figures are typical:

Phosphoric acid	11–23%
Silicic acid	3–13
Calcium oxide	38–59
Ferrous and ferric oxides	6–25
Protoxide of manganese	1–6
Alumina	0.2–3.7
Magnesia	2–8
Sulphur	0.2–1.4

The fertilizing value of the slag was not recognized for a long time. A considerable portion of its phosphoric acid was found to be soluble in dilute citric and carbonic acids, which led to successful field experiments. The only preparation of the slag for fertilizer purposes when its value was first recognized, consisted in having it finely ground in

specially prepared mills so that 75 per cent would pass a sieve of 0.17 mm. mesh. This requirement was suggested by M. Fleischer, who used the slag with much success in improving marsh and meadow lands.

Previous to 1890, by means of pot, as well as by laboratory experiments, Wagner demonstrated that the phosphoric acid in different slags of the same degree of fineness, varied in its availability from 30 to 90 per cent, and further that many brands were adulterated with Belgian and other insoluble phosphates. The value is now determined by finding the percentage of phosphoric acid soluble in a 2 per cent citric acid solution, and these results are found to approximate very closely the results obtained by pot experiments.

The form in which the phosphoric acid exists in the slag has never been fully explained. It was formerly supposed that it was combined with lime as a tetracalcium phosphate and that this latter compound being less stable than tricalcium phosphate, under the influence of dilute acids became easily available to the plants by being decomposed into the calcium salt of the dissolving acid, and ticalcium phosphate. The tetracalcium phosphate, however, has never been made artificially, although it has been recognized under the microscope in the slag and exists as a mineral under the name of Isoklas.

More recent investigations have shown, as already indicated, that those slags of like phosphoric acid content which are richest in silicic acid give the best results. Hence the conclusion has been drawn that a part of the lime must be in the form of silicate. It is now generally held that the phosphoric acid is combined in the slag as a double salt of tricalcium phosphate and calcium silicate and that in this form the roots are able to utilize it. It is also believed that some of the phosphoric acid is more or less united with iron as a basic iron phosphate.

Bone. Bones consist of two distinct kinds of matter. One is mineral in character and consists of phosphate of lime or true bone phosphate; the other is organic, consisting of a flesh-like matter called ossein, which contains much nitrogen. An average analysis of bones is as follows:

Moisture	34.20%
Mineral matter (ash)	22.80
Fats	20.50
Albuminoids	20.60
Undetermined organic matter	1.90

The ash contained

Calcium phosphate	87.40%
Calcium carbonate	11.50
Undetermined mineral	1.10

Bones as a source of phosphoric acid for fertilizer manufacture come on the market in several forms. In large packing houses or in

localities where large amounts of bone can be collected, they are treated for the extraction of the gelatine, of which they contain about 33 per cent. To extract the gelatine the bones are steamed in tanks under 40 lbs. pressure for three or four hours. The gelatine being dissolved and the grease liberated, rises to the top. The grease is skimmed off and the liquor containing the gelatine drawn off for further treatment The bones with some meat still adhering are removed from the tanks dried and ground, producing "steamed bone meal." This contains from 4 to $4\frac{1}{2}$ per cent ammonia and 22 to 24 per cent bone phosphate. If steamed at a pressure of 50 to 60 lbs. and for a longer time, more of the gelatine is removed and the meal runs correspondingly lower in ammonia. Raw bone is bone that has been boiled in open kettles to remove the grease and gelatine; this method, however, is not so efficient as steaming under pressure and the bone meal runs higher in ammonia and lower in phosphoric acid.

Bone Black. For use in sugar refining, bones are calcined until black and brittle. This removes all the organic matter and renders them very porous. After their value to the sugar refiner is gone, they are sold to the fertilizer manufacturer as bone-black, containing about 30 to 35 per cent phosphoric acid and no ammonia.

Part of the phosphoric acid in steamed or raw bone meal is in the available form. This class of bone is a very good fertilizing material as the phosphoric acid is decomposible in the ground and in the course of four or five years is rendered all available, thus furnishing a steady supply of phosphoric acid to plant growth. The phosphoric acid of bone-black or bone ash is, however, entirely unavailable without treatment with acid. Superphosphate and dissolved bone-black are terms applied to the bone meal and bone-black which have been acidulated so that the phosphoric acid is rendered available for plant growth.

Chemistry of the Manufacture of Acid or Super-phosphate. The reaction which takes place on the addition of sulphuric acid to phosphate rock or bone is as follows:

$$3Ca_3(PO_4)_2+6H_2SO_4+12H_2O=4H_3PO_4+Ca_3(PO_4)_2+6CaSO_4\cdot 2H_2O$$

and

$$4H_3PO_4+Ca_3(PO_4)_2+3H_2O=3CaH_4(PO_4)_2\cdot H_2O$$

A simpler form of the reaction is expressed as follows:

$$Ca_3(PO_4)_2+2H_2SO_4+5H_2O=CaH_4(PO_4)_2\cdot H_2O+2CaSO_4\cdot 2H_2O.$$

If 310 parts by weight of finely ground tricalcic phosphate be mixed with 196 parts of sulphuric acid and 90 parts of water, and the resulting jelly is quickly diluted with water and filtered, there will be found in the filtrate about three-quarters of the total phosphoric acid as free acid. If, however, the jelly at first formed as above, is left to become dry and

hard, the filtrate, when the mass is beaten up with water and filtered, will contain monocalcic phosphate $CaHPO_4$.

If the quantity of sulphuric acid used is not sufficient for complete decomposition, the dicalcium salt is formed directly according to the following rêaction:

$$Ca_3(PO_4)_2+H_2SO_4+6H_2O=Ca_2H_2(PO_4)_2\cdot 4H_2O+CaSO_4\cdot 2H_2O.$$

This arises doubtless by the formation at first of the regular monocalcim salt and the further reaction of this with the tricalcium compound as follows:

$$CaH_4(PO_4)_2+H_2O+Ca_3(PO_4)_2+7H_2O=2Ca_2H_2(PO_4)_2\cdot 4H_2O.$$

This reaction represents, theoretically, the so-called reversion of the phosphoric acid. When there is an excess of the sulphuric acid there is a complete decomposition of the calcium salts with the production of free phosphoric acid and gypsum. This reaction is represented as follows:

$$Ca_3(PO_4)_2+3H_2SO_4+6H_2O=2H_3PO_4+3[CaSO_4\cdot 2H_2O.$$

The crystallized gypsum absorbs the 6 molecules of water in its structure.

Reactions with Fluorides. Since calcium fluoride is present in nearly all mineral phosphates, the reactions of this compound must be taken into consideration in the chemistry of this subject. When treated with sulphuric acid the followng reaction takes place:

$$CaF_2+H_2SO_4=2HF+CaSO_4.$$

The free HF then reacts with any silica present as follows:

$$4HF+SiO_2=2H_2O+SiF_4.$$

This compound however is decomposed at once in the presence of water, forming hydroflousilicic acid, as follows:

$$3SiF_4+2H_2O=SiO_2+2H_2SiF_6.$$

The presence of fluorides is very objectionable both on account of the dangerous gases evolved during the manufacture and because 100 lbs. of calcium fluoride will consume 125.6 lbs. of the sulphuric acid.

Reaction with Carbonates. Most mineral phosphates contain carbonates in varying quantities. On treatment with sulphuric acid these are decomposed as follows:

$$CaCO_3+H_2SO_4=CaSO_4+H_2O+CO_2.$$

When present in only moderate quantities they are not objectionable as the reaction produces a rise in temeprature throughout the mass, and the CO_2 formed permeates and lightens the whole mass, assisting thus in completing the reaction by leaving the mass porous, and capable

of being easily dried and pulverized. When large quantities are present however, additional water should be added to furnish the proper amount for the crystallization of the gypsum. 100 parts by weight of calcium carbonate require 125 parts of 60° Bé. acid.

Solution of the Iron and Alumina Compounds. Iron may occur in mineral phosphates in many forms. It probably is most frequently present as ferrous or ferric phosphate, seldom as oxide and often as pyrite. The alumina is chiefly present as phosphate and as silicate. When, as is generally the case, a little less sulphuric acid is employed than is necessary for complete solution, the iron phosphate is attacked as follows:

$$3FePO_4+3H_2SO_4=FePO_4\cdot 2H_3PO_4+Fe_2(SO_4)_3.$$

A part of the iron sulphate formed reacts with the acid calcium phosphate present to produce a permanent jelly-like compound, difficult to dry and handle. By careful practice as much as 4 to 6 per cent may be handled, but over 2 per cent is objectionable. Pyrite and silicate are not attacked by the sulphuric acid and these compounds are therefore not objectionable and no account is taken of them in analyzing phosphates.

With sufficient acid the alumina phosphate is decomposed with the formation of aluminum sulphate and free phosphoric acid, as follows:

$$AlPO_4+3H_2SO_4=Al_2(SO_4)_3+2H_3PO_4.$$

Reaction with Magnesium Compounds. The mineral phosphates, as a rule, contain but little magnesia. When present it is probably as an acid salt, $MgHPO_4$. Its decomposition takes place in slight deficiency or excess of sulphuric acid respectively as follows:

$$2MgHPO_4+H_2SO_4+2H_2O=[MgH_4(PO_4)_2\cdot 2H_2O]+MgSO_4.$$

and

$$MgHPO_4+H_2SO_4=H_3PO_4+MgSO_4.$$

The magnesium, when present as oxide, is capable of producing a reversion of the monocalcic phosphate as follows:

$$CaH_4(PO_4)_2+MgO=CaMgH_2(PO_4)_2-H_2O.$$

One part by weight of magnesia can render 3½ parts of soluble monocalcic phosphate insoluble.[1]

Wood and Lime Kiln Ashes. These are chiefly valuable as fertilizer materials on account of the potash they contain. A good grade of unleached wood ashes should contain about 5 to 6 per cent potash, while the lime kiln ashes will run slightly lower. They both contain about 2 per cent phosphoric acid.

Tobacco Stems and Dust. These contain ammonia, phosphoric acid, and potash, the latter being the highest. Stems will run 2 to 3

[1] From Prin. and Practices Agric. Analysis. H. W. Wiley.

per cent ammonia, and 7 to 8 per cent potash. The dust runs slightly higher in ammonia and from 2 to 3 per cent potash. Both carry small amounts of phosphoric acid. Tobacco dust is valuable as a filler on account of its absorbent properties.

Cotton-seed Meal Ashes. This material contains about 10 per cent total phosphoric acid, 8 per cent available phosphoric acid and 17 to 18 per cent potash.

Night Soil. The material collecting in cesspools is pumped upon sandy soil, where it is allowed to dry. This is used locally and constitutes a valuable fertilizer.

How to Calculate Amounts of Material to be Used in Making a Complete Fertilizer of Definite Composition from the Raw Materials. Suppose that we desire to make a fertilizer having the composition: nitrogen 4 per cent, phosphoric acid 8 per cent, and potash 10 per cent. Suppose in addition that we have on hand the following materials: nitrate of soda containing 16 per cent nitrogen, acid phosphate containing 15 per cent available phosphoric acid, and muriate of potash containing 50 per cent actual potash (K_2O). How many pounds of each of these materials will we require?

To contain 4 per cent nitrogen, the ton must contain 80 lbs. Nitrate of soda contains 16 lbs. of nitrogen in every 100 of the nitrate, and hence 500 lbs. of nitrate of soda would be required to make up the 80 lbs.

To contain 8 per cent phosphoric acid, the ton must contain 160 lbs. The phosphate contains in every 100 lbs. 15 lbs. of phosphoric acid and hence 1067 lbs. of the acid phosphate will be rquired to furnish 160 lbs. available phosphoric acid.

To contain 10 per cent potash the ton must contain 200 lbs. Our muriate contains in every 100 lbs. 50 lbs. actual potash, and hence 400 lbs. will be required to give the 200 lbs.

We should then have the following:

500 lbs. nitrate of soda,
1067 lbs. acid phosphate,
400 lbs. muriate of potash,

or a total of 1967 lbs. Now to make it up to one ton we simply add 33 lbs. of any inert material such as dirt for instance, and we then obtain one ton of fertilizer of the desired composition. By adding one more ton of "filler" we should have two tons of fertilizer of the following composition: nitrogen, 2 per cent, phosphoric acid, 4 per cent, and potash, 5 per cent.

Now for a more complicated example suppose we wish to make a fertilizer of the same composition, but instead of having three materials, each containing only one ingredient, suppose we have on hand Peruvian guano, containing 3 per cent nitrogen, 18 per cent phosphoric acid, and 3½ per cent potash.

To give us 160 lbs. (8 per cent) of phosphoric acid we shall require about 900 lbs. of this guano. Nine hundred pounds would also supply 27 lbs. of nitrogen and 31 lbs. of potash. But we require 80 lbs. of nitrogen and 200 lbs. of potash in all, or 53 lbs. more nitrogen and 169 lbs. more potash to complete the mixture. Three hundred and eighty-four pounds of nitrate of potash analyzing 14 per cent nitrogen and 44 per cent potash would supply this 53 lbs. nitrogen and also the 169 lbs. potash, therefore we have

		Nitrogen.	Phos. Acid.	Potash.
	900 lbs. guano containing	27 lbs.	160 lbs.	31 lbs.
and				
	384 lbs. nitrate of potash	53 lbs.		169 lbs.
or total of				
	1284 lbs. containing	80 lbs.	160 lbs.	200 lbs.

now by adding 716 lbs. of filler we have one ton of fertilizer of the desired formula.

For a third example, suppose we have the following materials:

1st. one containing 3 per cent nitrogen, 18 per cent phos. acid, and 3½ per cent potash
2d. one containing 6 per cent nitrogen, 9 per cent phos. acid and 2 per cent potash
3d. one containing 50 per cent potash

we would then take

		Nitrogen.	Phos. Acid.	Potash.
1st.	300 lbs. containing	9 lbs.	54 lbs.	10 lbs.
2d.	1200 lbs. containing	72 lbs.	108 lbs.	24 lbs.
3d.	332 lbs. containing			166 lbs.
Total	1832	81	162	200

By adding 168 lbs. of filler we then have one ton of our fertilizer.

A filler in common use is obtained from garbage extracted for the grease which it may contain. The pressed and dried material has practically no value from its nitrogen or phosphorous content although the tankage is very heavy in soluble material.

Peat Filler. Dried humus or peat is used as a filler on account of its absorbent properties, but its use is prohibited by some states if the nitrogen content is included in the nitrogen of the fertilizer, because this nitrogen is unavailable.

XXI

ILLUMINATING GAS

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Classification. The industrial gases in use at the present time may be divided, roughly, into three general classes—coal and carburetted water gas and their various mixtures; the different classes of oil gas, acetylene, gasoline gas; and producer gas. The first class is by far the most important from an illuminating standpoint, while producer gas is, of course, of the greatest importance for fuel and power use. The other gases are generally employed in special cases where the use of the first class is impossible or inconvenient.

Development. In the earlier days of the development of the industry, gas was employed primarily as an illuminant, and to the present day the illuminating value is usually the standard prescribed by regulations, but there is a tendency, which was started in Germany and in England, to discard to some extent the illuminating standard and to substitute for it a standard of heating value.[1]

In spite of the increase in competition of electricity for illumination and its use in many forms of heating and power purposes, the gas industry as a whole has shown a steady and constant increase. The preliminary figures of the late census which give the data available for the year 1909, bear this out.

GAS, ILLUMINATING AND HEATING

	1909.	1904.	% increase.
Number of establishments	1,296	1,019	27
Capital	$915,537,000	$725,035,000	26
Cost of materials used	52,428,000	37,180,000	41
Salaries	12,385,000	8,464,000	46
Wages	20,931,000	17,058,000	23
Miscellaneous expenses	27,757,000	29,557,000	−6
Value of products	166,814,000	125,145,000	33
Value added by manufacture	114,386,000	87,965,000	30
Numbered of salaried officials	13,515	9,406	44
Average of wage earners employed	$37,215	$30,566	22
Primary horse-power	128,350	73,101	76

[1] One reason for this being the increasing use of the Welsbach light, which depends on the heating value alone for its efficiency.

PRODUCTS. KIND AND QUANTITY

Total gas, M's of cubic feet	150,835,793	112,549,979	34
Straight coal gas	19,985,253	12,693,034	57
Straight water gas	1,726,082	715,550	141
Carburetted water gas	79,418,486	54,687,418	45
Mixed coal and water gas	40,775,283	40,980,414	−1
Oil gas	8,688,860	3,441,352	152
Acetylene gas	25,186	7,881	220
All other gases	216,643	24,330	790
Coke, bushels	82,049,683	89,146,434	−8
Tar, gallons	92,152,938	67,515,421	36

ESTIMATED TOTALS INCLUDING COKE OVEN GAS

Water gas (blue and carburetted)	103,000,000,000 cu.ft.
Coal gas (retort, by-product)	57,000,000,000 "
All other gases (oil, acetylene, etc.)	9,000,000,000 "
Total manufactured gases	169,000,000,000 "

ESTIMATED TOTAL RESIDUALS

Coke	8,500,000 short tons
Tar	152,000,000 gallons
Ammonia as such	49,000,000 pounds

Constituents of Illuminating Gas. Commercial gases consist of mixtures, in varying proportions, of the gases or vapors whose characteristics are shown in the following table:

PROPERTIES OF THE IMPORTANT CONSTITUENTS OF COMMERCIAL GASES[1]

Name.	Specific Gravity	Weight per Cu. Ft. Lbs.	Specific Heat.	Heating Value. B.T.U. per Cu. Ft.	Heat of Formation B.T.U. per Lb.	Air Required for Cu. Ft., per Cu. Ft.	Combustion. Lbs. per Lb.	Flat Flame Candle Power Burned at 5 Cu. Ft. per Hour.
Benzol	2.6953	.20640	.3754	3807.5	− 229.3	35.888	13.313	350–420
Ethylene	.9676	.07410	.4040	1588.0	− 174.2	14.355	14.836	68.5
Hydrogen	.0692	.00530	3.4090	326.2	....	2.393	34.624	
Carbon monoxide	.9671	.07407	.2450	323.5	+1869.2	2.693	32.471	
Methane	.5529	.04234	.5929	1009.0	+2435.6	9.570	17.312	5.2
Ethane	1.0368	.07940	.7070	1764.4	+1713.6	16.748	16.156	35.7
Carbon dioxide	1.5195	.11637	.2163	....	+3979.1			
Oxygen	1.0152	.08463	.2174					
Nitrogen	.9701	.07429	.2438					
Air	1.0000	.07658	.2374					
Steam	.6217	.04761	.4805	....	+6870.4			
Hydrogen sulphide	1.1769	.09012	.2423	672.2	+ 250.9	7.178	6.111	
Ammonia	.5888	.04509	.5083	432.8	+1259.0	3.589	6.111	
Cyanogen	1.8000	.13779	.2615	1238.2	−2273.9	9.570	5.323	
Carbon disulphide	2.6298	.20139	.1590	1264.6	−6160.0	14.355	5.466	

[1] The data given are calculated to 60° F. and 30.0" Barometer.

In addition to the constituents shown in the table, there always exists in the crude gases, before purification, traces of ammonia and other organic compounds, but the above mentioned constituents may be considered as those important to the industrial chemist.[1]

The relative occurrence of the commoner constituents in some of the many varieties of commercial gases is given in the table below. These typical analyses must not be considered as standards, but rather expressing the average composition of commercial samples as obtained under certain conditions with the process mentioned.

AVERAGE COMPOSITION OF COMMERCIAL GASES

	Ill.,s %	CO %	H_2 %	CH_4 %	C_2H_6 %	CO_2 %	O_2 %	N_2 %	C.P. %	B.T.U. %
Coal gas	4.0	8.5	49.8	29.5	3.2	1.6	.4	3.2	16.1	622
Carb. water gas	13.3	30.4	37.7	10.0	3.2	3.0	.4	2.1	22.1	643
Pintsch gas	30.0	.1	13.2	45.0	9.0	.2	.0	1.6	43.0	1276
Blau gas	51.9	.1	2.7	44.1	.0	.0	.0	1.2	48.2	1704
All oil water gas	7.0	9.2	39.8	34.6	......	2.6	.2	6.6	19.7	680
Acetylene gas	96.0	....	....	......	......	....	.8	3.2	225.0	1350
Gasoline gas	1.5	....	....	C_6H_{14} = 10.3			18.5	69.7	16.0	514
Oil gas	31.3	2.4	13.5	46.5	3.9	.3	.0	1.1	38.0	1320
Blue water gas	.0	40.9	50 8	.2	.0	3.4	.9	3.5	......	299
Ballon gas	.4	5.2	75.4	10.4	.0	1.0	.6	.7	......	375
Methane-hydrogen gas	3.0	15.0	64.2	12.0	.0	2.3	.2	3.0	11.0	400
Producer gas (coal)	.2	17.6	10.4	6.3	.0	7.3	.7	58.1	......	161
Producer gas (coke)	.0	25.3	13.2	.4	.0	5.4	.6	55.2	......	137
Blast furnace gas	.0	26.5	3.5	.2	.0	12.8	.1	56.9	......	100
Wood gas (pine)	10.6	27.1	32.7	21.5	......	4.9	.4	2.6		607

In general, then, we may say that the commercial gases are mixtures of gases, hydrocarbons and vapors, together with certain permanent gases produced by the pyrodecomposition and polymerization of complex hydrocarbon mixtures or compounds either alone or in the presence of air and steam.

[1] State Commissions, M.E., Sept., 1910, p. 222; E.W., Feb. 3, 1910, p. 226; E.W., Aug. 5, 1910, p. 291.

Regulations and Testing: A.G.L.J., Aug. 5, 1907, p. 227; L.J., Nov. 27, 1906, p. 601; L.J., March 7, 1906, p. 647; G.W., Aug. 6, 1904, p. 233; P.A., July 1, 1904, p. 319.

Photometric and Heating Value: G.W., Feb. 18, 1911, p. 192; L.J., April 22, 1911, p. 227; L.J., Sept. 28, 1909, p. 831; G.W., June 16, 1909, p. 72; L.J., July 13, 1909, p. 199; L.J., Oct. 13, 1909, p. 117; P.A., Sept. 15, 1908, p. 559.

Sulphur Regulations. P.A., June, 1, 1911, p. 473; L.J., Dec. 27, 1910, p. 928; G.W., Dec. 4, 1909, p. 707; P.A.C.I., 1909, p. 453.

Mechanical Coal and Coke Handling Devices.[1] The installations and mechanical means for handling the coal and coke from the storage pile to the retort house have been very general. Telfor systems have been considerably used, yet the belt and bucket type of conveyor system for handling coal, and the push plate conveyor running in a trough for coke, seem to be found in most general use. Figs. 215, 216, and 217 illustrate a typical system and show the course of the coal from the dock to the storage bins over the retorts. Formerly the coal was shoveled into the retorts by hand, and when carbonized was withdrawn with rakes. As the plants increased in size mechanical forms of both charging and

FIG. 215.—Unloading Coal at Dock and Dumping into Trucks.

discharging machines were brought out; a number of commercial types of such machines are illustrated. For the short, single end retorts the Bronder machines, Fig. 218, have been successfully used. For the various types of through retorts where the retort varies from 18 to 22 ft. in length, the Fiddes-Aldridge machine, Fig. 219, which simultaneously

[1] Charging and Discharging Machines: L.J., July 31, 1906, p. 306; L.J., June 26, 1906, p. 900; G.W., June 16, 1906, p. 1191; L.J., Jan. 9, 1906, p. 103; L.J., Aug. 29, 1905, p. 557; L.J., May 17, 1904, p. 436.

Coal Handling Machinery: L.J., Jan. 17, 1911, p. 161; L.J., Aug. 2, 1910, p. 319; E.W , July 7, 1910, p. 23; L.J., May 31, 1910, p. 553; G.W., March 12, 1910, p. 318; L.J., June 29, 1909, p. 973; P.A.G.I., 1909, p. 503; P.A., May 15, 1909, p. 418; L.J., Feb. 9, 1909, p. 373; P.A., Aug. 1, 1906, p. 480.

Fig. 216.—The coal having been dumped into hopper from trucks is crushed and transferred to bucket conveyors.

Fig. 217.—This illustration shows the buckets loaded and on their way to the storage bins.

pushes out the coke charge and at the same time deposits the fresh charge of coal, the West machine, Fig. 220, which uses scoops, and the De Brower, Figs. 221 and 222, which utilizes centrifugal force, have all been developed for charging the coal into the retort. After carbonizing, the coke is pushed out with some form of collapsible ram.

Manufacture of Coal Gas. Fig. 223 illustrates what is known as a " bench " and consists of 6 to 8 fireclay vessels, " retorts" ranging from 8 to 18 ft. in length, about 18 inches wide and 15 inches high.

Each retort is filled with its charge of coal, the cast-iron door closed and clamped into position. The heat is now applied either by means

FIG. 218.—This illustration shows the conveyor as it passes over the retorts. The machine below is the Bronder Discharging Machine. This discharges three retorts simultaneously with "T" headed rakes, operated with a steam cylinder. Used for stop-end retorts.

of coal in the older system, or by a regenerative method in the modern plants. These retorts may be set either in a horizontal or inclined position, but in the latter case the method of charging and discharging is different from that given above. The object, however, in any case is to drive off the volatile matter which consists principally of gas. Other products are also eliminated, and will be considered in due course of time.

The manufacture of coal gas thus consists in the transformation of the potential energy of a set of solid hydrocarbons into the more convenient gaseous form by means of dry distillation. Murdock, who is probably the inventer of coal gas, distilled the coal in a simple

iron pot over a fire, and to a certain extent this is still the basic principle of our present day practice.

Many other methods of carbonizing have been proposed and tried. These may be classed under three heads, viz.: (*a*) the use of internally heated vessels; (*b*) the use of a body of ignited coke; and (*c*) the use of hot gas as a heat carrier.

Many patents have been taken out and a great deal of experimental work has been done in endeavoring to perfect processes that would utilize these principles, but in general they have failed to produce a gas that could commercially compete with that produced in the usual

FIG. 219.—Fiddes Aldridge One-stroke Machine. The charging scoop is sectional and pushes the coke out of one end of the retort as it enters with the fresh charge at the other end.

system of carbonizing the coal in an externally heated retort. The principal causes of their failure have been the time required for the complete distillation of the coal and the poor quality of gas produced, due, generally, to its decomposition in the presence of the high temperatures that were necessarily employed.

There are three general methods by which the distillation of coal in externally heated closed retorts is carried on:

First, the use of relatively small charges of coal which do not completely fill the enclosing retort, leaving a variable free space at the top. This would represent the usual horizontal or inclined retorts.

FIG. 220.—West Charging Machine, operated with steam supplied by a trolley system. Charges three retorts simultaneously. Scoops carry coal into retort and fingers hold it in place while scoop is withdrawn.

FIG. 221.—De Brower-Jenkins Discharging Ram. Electrically operated. Is raised and lowered to take retorts at different levels.

Second, the use of relatively large thick charges of coal which do not completely fill the retort and leave a free space at the top, such as a chamber or coke oven.

Third, the use of vertical retorts where the whole periphery is heated and filled with the charge, but there may or may not be a free space above the charge at the top of the retort. This type includes the various continuous or intermittently charged vertical retorts and some of the modifications of the vertical coke oven.

A number of the different commercial modifications of apparatus designed to operate under the methods just described are represented in Figs. 223, 224, 225, 226, and a modern example of each type will be described. It will be noted that all of these forms are heated by producer gas, generated either in producers built as an integral part of the bench or in separate plants. The proper and efficient operation of a producer, and the maintaining of a uniform and effective temperature in the carbonizing chambers, are the important factors in successful bench operation.[1]

The advances that have been made in recent years in the efficiency of many of our manufacturing processes are based on the great advance we have made in our knowledge of the mechanism of combustion, and in the refinements and methods for its accurate control.

Fig. 222. — De Brower-Jenkins Centrifugal Charging Machine. Electrically operated. Has elevating conveyor to pick up coal from the charging floor level, which does away with elevated bins.

The important factors in the operation of the producer are proper

[1] Through Horizontal: P.A., April 15, 1910, p. 341; P.A.G.I., 1909, p. 352, p. 398.

American Verticals: P.A.G.I., 1909, p. 393; P.A.G.I., 1908, p. 550.

Dessau Verticals: L.J., June, 20, 1911, p. 851; P.A., March 15, 1911, p. 232; L.J., April 19, 1910, p. 167; L.J., Jan. 4, 1910, p. 27.

Glover-West Verticals: L. J., June 20, 1911, p. 859; L.J., Aug. 16, 1910, p. 454; L.J., Nov. 2, 1909, p. 316; G.W., Sept. 25, 1909, p. 354.

Wordall-Duckham Verticals: L.J., June 20, 1911, p. 857; P.A.G.I., 1908, p. 384.

Chamber Ovens: L.J., Aug. 9, 1910, p. 388; L.J., June 28, 1910, p. 949; L.J., May 26, 1908, p. 502.

Coke Ovens: P.A., May 1, 1911, p. 364; L.J., June 25, 1907, p. 975.

regulation of the drafts and the admission at a uniform rate of the requisite quantities of primary and secondary air required in order that a suitable temperature may be maintained, and to insure the efficiency of this combustion the flue gases must contain a high

FIG. 223.—American Type of Vertical Retort. Nine retorts in bench. Retorts oval, 10″×14″ at top, 16″×22″ at bottom, 18′ 6″ long. One producer of large grate area. Primary and secondary air controlled with Venturi meters. Three retorts on one standpipe, which are charged and discharged at one time. Length of charge 9 hours, coal and coke handled by conveyors. Electrical operation.

percentage of carbon dioxide. Accurate commercial instruments are now available for the determination and the control of all of these factors.

The introduction of external producer plants, where the gas is generated and partially purified before being admitted to the benches, seems to promise further economies in the fuel necessary to carry out the

process of carbonization. Other mechanical devices have been introduced, such as rocking grates, which are designed to continuously remove the ash and thus result in more uniform fire conditions, and mechanical devices whereby the admission of the primary and secondary air may be controlled to correspond to the varying conditions of the fuel bed.[1]

FIG. 224.—Venturi meters controlling air supply to coal gas benches.

[1] General Theory: Le Genie Civil, April, 23, 1910; L.J., Jan. 8, 1907, p. 89; P.A.G.I., 1907, p. 740 et seq.

Construction: A.G.L.J., Feb. 7, 1910; p. 243, A.G.L.J., Sept. 27, 1909, p. 763; A.G.L.J., July 6, 1903, p. 5 et seq.; P.A., April, 1,1903, p. 151 et seq.

Operation and Appliances: G W., Feb. 8, 1911, p. 199; G.W., May 21, 1910, p. 639; J.S.C.I., March 15, 1910, p. 261; L.J., Oct. 13, 1908, p. 132; L.J., July 28, 1908, p. 254; P.A.G.I., 1907, p. 792; L. J., July 30, 1907, p. 310 et seq.; G.W., Nov. 10, 1906, p. 936; P.A., July, 2, 1906; p. 412; L.J., June 27, 1905, p. 957 et seq.; G.W., June 5, 1905, p. 1033; G.W., Jan. 14, 1905, p. 59; P.A.G.L. Ass., 1901, p. i.

The saving in fuel that has been effected by the use of more accurate control over the combustion is shown by the following table, where the fuel used in the producer, when calculated to pounds of coke per thousand feet of gas made, is compared:

Type of Bench.	Fuel in Lbs. per M feet Gas Made.
Old type of direct fired	70 to 75 lbs.
Full depth recuperative bench without mechanical control	30 to 35 lbs.
Mechanically controlled benches	18 to 22 lbs.

FIG. 225.—Glover-West Continuous Verticals. Sectional elevation of vertical retort house and coal stores. Eight retorts in a bench. Single producer. Retorts are heated by sections. Coal falls into retort by gravity as coke is removed from the bottom.

Gas Coal. In the manufacture of coal gas, coal with a high volatile content is generally preferred; that is, a coal belonging to the bituminous series according to the usual method of coal classification. These methods of classification vary somewhat, but usually depend either on the ratio of volatile combustible to fixed carbon, or upon the ratio of hydrogen to carbon, as determined by ultimate analysis. Such a classification is given in the table on the following page.

COAL CLASSIFICATION—GRUNER

	Carbon.	Hydrogen.	Oxygen.
Dry coal; long flaming, non-coking	75–80	4.5–5.5	15.0–18.5
Fat gas coal; porous, brittle coke	80–85	5.0–5.8	10.0–13.2
Semi-fat furnace coal; good coke but porous	84–89	5.0–5.5	5.5–10.0
Coking coal; best grade of coke	89–91	4.5–5.5	4.5–5.5
Lean and anthracite coals; non-coking	90–93	3.0–4.5	3.0–4.5

The gas coals in general use have a volatile content running from 32 to 40 per cent or a carbon hydrogen ratio of from 13½ to 17. The analyses of a number of American coals are shown in the table:

PROXIMATE AND ULTIMATE ANALYSES OF GAS COALS

State. Coal.	Penna. Pittsburg.	W. Virginia. Fairmont.	Kentucky. Straight Creek.	Ohio. Hocking Valley.	Ind. Ter. Hartshorn.
Moisture	1.07	1.35	1.92	6.72	3.87
Volatile matter	39.24	36.92	36.56	37.13	35.73
Fixed carbon	50.92	55.36	57.08	50.32	50.05
Ash	8.77	6.37	4.44	5.83	10.35
Carbon	82.47	78.31	78.31	69.42	69.85
Hydrogen	6.01	5.26	5.36	5.35	5.14
Oxygen	6.81	7.61	8.80	16.27	11.38
Nitrogen	1.88	1.55	1.85	1.46	1.29
Sulphur	2.83	.90	1.24	1.67	1.99
Heating value, B.T.U. per pound	15353	14164	14319	12388	12620

The result of distilling coal at various temperatures has been quite carefully studied by a number of observers, and it has been found that not only the percentage of the volatile matter, but its composition plays an important part.

It is notable that some of the newer Western coals yield considerably less gas than the Eastern coals having the same content of volatile matter. The ultimate analysis of a coal does not throw very much light on its suitability for the manufacture of gas, although certain general indications may be derived from it. In general, increasing percentages of hydrogen result in more volatile constituents, and high percentage of oxygen apparently decreases the yield of gas and slightly increases the yield of tar. The higher percentages of nitrogen usually result in more ammonia. The presence of sulphur is to be avoided as far as possible, yet its manner of occurrence is important in determining whether it will be volatile and go off in the gas and have to be removed, or whether it will remain in the coke. Where the coke is to be used for the manufacture of water gas, the composition and fusing point of the ash is important, while in case it is to be used for foundry work, the absence of sulphur and phosphorus is essential.[1]

[1] Nature of Reaction: J. für G., Sept. 1, 1906, p. 741 et seq.; Compt. Rendu, X, Int. Gas Cong., p. 239; B. à la S. à E., p. 7; Industrie, 1892, p. 319.

From the high temperatures and considerable amount of fuel that are employed in the distillation of coal we would expect to find an endothermic reaction, and it is still so considered by some. The work of Mahler, Euchane and others has shown that it is probably slightly exothermic. The heat given off by the distillation varies somewhat with the volatile content of the coal and other conditions, but averages about 350 B.T.U. per pound of coal.

The fuel used in carrying out the process serves to start the distillation and supply the sensible heat that is carried off by the evolved products.

FIG. 226.—Operating Floor and Charging Larry Vertical Retort House.

From the heat balance that is given in the table it will be noted that the heat given off by the reaction is but a small fraction of the total heat involved and may be neglected.

HEAT BALANCE WITH A REGENERATIVE BENCH

PER 100 LBS. OF COAL CARBONIZED

Heat Produced.

By combustion of coke	180553	B.T.U.
By formation of volatile compounds	52637	"
Total heat evolved	233190	"

Heat Absorbed.

As sensible and latent heat of flue gases	58734	B.T.U.
As sensible heat of gaseous vapors	32166	"
As sensible heat of coke	43148	"
As sensible heat of clinker	1863	"
By radiation	48276	"
By formation of volatile compounds	3517	"
By decomposition of coal	45486	"
Total heat absorbed	233190	"

PERCENTAGE DISTRIBUTION OF HEAT LOSSES

By flue gases	25.20%	
By volatile compounds	13.80	
By coke	18.50	
		57.50%
By radiation	20.70	
By formation of volatile compounds	1.50	
By decomposition of coal	19.50	
By clinker	.80	
		42.50%

It is interesting to note in this connection that in the example quoted the fuel used was at the rate of 30.2 lbs. per thousand cubic feet of gas made, almost exactly what we would expect in the manufacture of carburetted water gas where not only all the heat necessary for the reaction, but also about one-third of the total heat in the gas comes from the fuel.

The general course of the distillation of coal is influenced by a number of factors and these may be summarized into the general statement that under any given condition of temperature and pressure it is the rate at which the heat penetrates the coal particles and the time that the gaseous vapors are exposed to its influence that determines the course and results of the distillation.

The coal particles acquire the temperature of the retort by conduction, radiation, and from the passage of the heated vapors through the charge. The rate of carbonization toward the center of a charge has been estimated at from 1.0–1.5 inches per hour in horizontal retorts, 0.5–.06 inch in vertical retorts, and from 0.3–0.5 inch in coke ovens. The factors that influence the rapidity of heating are the available heat, head, the size of the coal particles and the moisture content. In general, in order to secure the maximum increase in temperature the coal particles should be brought into intimate contact with the walls of the retort, and must provide a certain percentage of voids for the circulation of the heated gases, while an increase in the size of the coal particles up to a certain point generally yields improved results.

The carbonization of the coal proceeds in three general stages:

First. There is a preliminary decomposition, which begins as soon as the coal has reached a temperature of from 350–400° C.; and as this stage is quite strongly endothermic, approaching as it does a fusion, the temperature remains practically constant until completion.

Second. The products resulting from the first stage, which consist principally of the higher members of the aliphatic series suffer molecular rearrangement with the formation of compounds containing probably less than three atoms of carbon. The first two stages take place almost simultaneously within the charge itself.

Third. The gaseous vapors resulting from the second stage when evolved from the protecting influence of the coal particles are acted upon by the conducted and radiant heat of the more highly heated portions of the charge proper, of the sides of the containing retort and of the highly heated surfaces with which the vapors may come into contact.

The reactions that take place during the third stage are very complicated and depend upon the temperature, time of contact and pressure. The influence of these factors are so intermingled that it is difficult to give each its true value as affecting the whole.

There results from the distillation of coal three classes of products: gases—condensed watery solutions—condensible hydrocarbons and a carbonaceous residue.[1]

These products are known commercially as coal gas—ammoniacal liquor—coal tar and coke. The average distribution of the elements in the coal into these products with their analysis is given in the tables below:

COMPOSITION OF COKE

	German.	English.	French.	American.
Carbon	84.76	90.75	84.35	81.34
Hydrogen	.90	.45	.67	.57
Oxygen	.34	1.50	1.35	2.40
Nitrogen	1.38	1.20	.40	.89
Sulphur	.93	.60	1.06	1.04
Ash	9.42	5.50	12.17	13.76
Moisture	2.27			

ELEMENTARY COMPOSITION OF COAL GAS

	Horizontal.	Vertical.	Coke Ovens.	French Hor.	English Hor.
Carbon	53.67	51.77	51.95	57.09	58.62
Hydrogen	21.04	20.86	19.15	19.45	22.37
Oxygen	16.43	17.56	13.05	19.65	15.34
Nitrogen	8.92	9.81	15.83	3.81	3.65

[1] For a general discussion of the theory of carbonization see P.A.G. I., 1908, p. 578, and P.R.S. A., Dec. 22, 1911, p. 135 et seq.

COMPOSITION OF COAL TAR

	Average.	Hydraulic.	Scrubber.	Condenser.	Holder.
Carbon	84.91	90.186	89.91	87.222	85.183
Hydrogen	9.65	4.848	4.945	5.499	5.599
Oxygen	3.50	4.966	6.279	6.279	9.218
Nitrogen	1.60				
Sulphur	.34				

DISTRIBUTION OF COMPONENTS OF COAL BY DISTILLATION

	Coal.	Coke.	Tar.	Gas.	Liquor.
Ash	8.18	8.18			
Moisture	4.34	......	......	......	4.340
Carbon	72.08	56.453	5.418	10.209	
Hydrogen	4.78	.446	.378	3.481	.475
Oxygen	8.73	.909	.504	3.516	3.800
Nitrogen	.87	.271	.042	.374	.183
Sulphur	1.02	.712		.308	....
Totals	100.00	67.071	6.342	17.888	8.799

GENERAL DISTRIBUTION OF PRODUCTS

FROM 100 LBS. OF COAL

Coal.	Horizontal. Yough.	Vertical. Westphal.	Coke Ovens. Dominion.	Munich Chambers. Saar.
Volatiles	34.8%	26.1%	34.6%	31.2%
Coke	68.6 lbs.	71.0 lbs.	71.13 lbs.	67.88 lbs.
Gas	18.4	16.3	16.43	15.60
Tar	7.8	4.58	3.38	6.19
Ammonia	.229	.326	.34	.239

If we should express the ultimate composition of these products as complex molecules the decomposition of the coal might be represented by the following equation:

$$\underset{\text{Coal}}{C_{357}H_{281}O_{39}} = \underset{\text{Coke.}}{C_{280}H_{26}O_8} + \underset{\text{Tar.}}{C_{27}H_{22}O_2} + \underset{\text{Gas.}}{5C_{10}H_{41}O_3} + \underset{\text{Water.}}{14H_2O}.$$

If the heats of combustion are calculated by the Dulong formula it will be found that the sum of the heats of combustion of the products is less by some 2.42 per cent than the heat of combustion of the coal, so that the reaction is exothermic by about 339 B.T.U. per pound of coal, which represents the heat liberated and thus lost during the distillation.

The relative occurrence of the constituents of these products is in general dependent upon the complex reactions that take place in the

third stage of the carbonization. As at the temperature of their formation these products are evolved as vapors we may consider them together and later discuss the different products formed by condensation.

The theory of the formation and molecular rearrangement of the various hydrocarbons under the influence of heat has been studied by a number of experimenters. The early theory propounded by Berthelot assumed that acetylene was the primary product of the pyrodecomposition and that all the products were the result of its condensation. Many other workers enlarged this idea, but from the more recent work we do not look for the primary formation of acetylene but rather expect a splitting off of the terminal hydrogen and carbon atoms with the formation of residues such as $H_2C=$ and $HC\equiv$ which according to the temperature and other conditions may combine with each other: take up hydrogen or decompose into their elements.[1]

The table below gives the general direction of the pyrocondensations at the lower and higher temperatures. It assumes that the simpler olifines and paraffines are the result of the first two stages of the carbonization and shows the probable products due to the influence of the higher temperatures that are effective during the third stage.

PROBABLE COURSE OF REARRANGEMENT OF HYDROCARBONS

Primary Products: Ethylene, methane, ethane and possibly hydrogen.

Ethylene → ethane+methane+hydrogen.
Ethane → acetylene+methane+hydrogen.
Acetylene → benzol.
Benzol → diphenyl, anthracene, phenanthene.
Benzol+acetylene → naphthalene.
Benzol+ethylene → styrolene and other tarry products.
Styrolene+benzol → naphthalene diphenyl. Acetnaphthalene, anthracene, and phenanthrene.

While the results given in the above table are from experimental data the tables below will give the results of actual conditions in carbonizing as affecting the composition of the gas, tar and coke at different periods of the distillation and under different temperature conditions.

[1] Decomposition of Coal: Bull. No. 32, University of Illinois, March 1, 1909; J.A.C.S., Sept. 1908, p. 1456; A.G.L.J., Oct. 12, 1908, p. 621; L.J., March 31, 1908, p. 823; J. für. G., July 25, 1908, p. 669 et seq.; Trans. C. S., 1908, 93, p. 1975; F. für. G., Aug. 4, 1906, p. 668; T.C.S., 1901, 79, p. 1042; F.C.S., 1897, 71, p. 41.

Theory of Hydrocarbons: A. de C. et P., v. 65–69; B., 1877, p. 853; B., 1878, p 1215; A.C., v. 189, p. 129; B., 1885, p. 859; J.f.G.,1886, p. 595; B.B., 1896, p. 2691; B.B., 1890, p. 84; J.A.C., 1899, p. 948; J.C.S., 1896, p. 377; J.f.G., 1906, p. 856; B.B., 1907, p. 2134; Z.A.C., 1907, p. 299.

RESULTS OF DIFFERENT CARBONIZING TEMPERATURES

Temperature	800° F.	1000° F.	1200° F.	1400° F.
Yield, cubic feet per pound	.409	1.233	2.319	3.601
Candle power	......	19.7	18.9	16.0
Candle feet	......	24.29	43.38	57.6
B.T.U.	523	651	745	626
Tar, gallons per ton	12.6	23.8	22.4	28.6
Coke, per cent	78.8	69.5	67.8	66.95
Volatiles in coke	22.04	13.00	7.97	5.88
Ammonia, pounds per ton	.37	1.47	2.29	3.71
Ills	6.00	5.85	5.75	4.50
CO	4.00	4.90	4.70	7.30
H_2	19.66	22.03	32.13	39.70
CH_4	18.45	30.78	36.53	37.30
C_2H_6	8.02	7.84	8.27	1.60
CO_2	7.80	6.00	3.45	3.20
O_2	.60	.30	1.20	1.35
N_2	35.47	23.23	7.97	5.05

The effect of the proper and regulated amount of superheating is well shown by the superior results obtained with the American type of vertical retorts which are not completely filled and the upper 4–5 ft. of the retort acts as a fixing chamber as against the German type in which the retort is completely filled and no fixing surface exists.

It will be noted that as the temperature rises and the time of exposure increases (due to the smaller make of gases) the change in the character of the products closely follows the direction that we should expect. It must be remembered in studying these results that the doubling of the volume of hydrogen as it is given off tends to mask the volumetric relations of the other hydrocarbons whose volume is not doubled and in some cases results in a contraction of volume.[1]

The pressure at which these reactions take place has a considerable influence on the products formed. Owing to the permeability of the retorts if too low a pressure is maintained furnace gases will be drawn in, which would seriously lower the candle power while on the other hand an excessive pressure, by retarding the evolution of the gas, tends to result in excessive decomposition and in the formation of graphitic

[1] Practical Tests: L.J., June 27, 1911, p. 1002; L.J., May 2, 1911, p. 308 et seq.; L.J., Jan. 31, 1911, p. 299; P.A., Oct. 1, 1910, p. 857; L.J., June 21, 1910, p. 836 et seq.; P.A., April 15, 1910, p. 341; L.J., Jan. 11, 1910, p. 96; P.A.G.I., 1909, p. 353.

Results: L.J., Sept. 6, 1910, p. 659; L.J., Jan. 11, 1910, p. 92; L.J., Dec. 14, 1909, p. 747.

Variation during Carborization: P. Eng. Cong., 1907; L.J., July 9, 1907, p. 99; A.G.L.J., Dec. 16, 1907; L.J., June 27, 1905, p. 955; L.J., Dec. 10, 1889, p. 1111; L.J., Feb. 14, 1888, p. 281; L.J., March 15, 1887, p. 491.

Retort House Governors: L.J., Sept., 20, 1910, p. 779; P.A., March 1, 1910, p. 160; G.W., Aug. 8, 1908, p. 157; L.J., April 3, 1906, p. 37.

carbon. Experience points generally to a balanced pressure just equal to that of the atmosphere and it should be maintained as nearly constant as possible. This latter condition is probably best insured by the use of retort house governors.

VARIATIONS DURING DISTILLATION

Vertical Retorts

Hours after Charging	1st	2d	3d	4th	5th	6th	7th	8th	9th
Proportion of yield	16.8	14.1	13.0	11.9	11.7	11.2	9.6	6.5	5.2
Candle power	20.7	20.2	19.5	17.9	15.0	12.9	8.1	1.9	
Heating Value	701	765	707	678	625	597	542	446	400
Ammonia, grains per 100 cu.ft.	540	440	380	250	250	250	130	70	40
H_2S, grains per 100 cu.ft.	510	470	430	295	285	260	180	100	50
Ills	8.05	8.00	7.70	5.60	4.10	3.60	2.80	.80	.30
CO	8.90	7.20	8.40	8.60	7.05	8.60	7.70	7.60	6.30
H_2	38.25	37.80	36.80	39.00	44.15	45.80	57.40	66.90	68.80
CH_4	38.45	39.60	41.30	42.00	39.60	37.40	27.00	20.70	18.60
C_2H_6	3.00	2.70	1.70	1.30					
CO_2	1.95	2.85	2.40	2.20	1.95	2.50	1.80	1.90	2.70
O_2	.40	.20	.20	.15	.55	.20	.30	.30	.80
N_2	1.00	1.65	1.50	1.15	2.60	1.90	2.00	1.80	2.50

In addition to the other gases which have been considered, there are present ammonia, cyanogen, hydrogen sulphide, carbon disulphide and traces of some other organic sulphur compounds that need not be considered. The ammonia and hydrogen sulphide both appear early in the distillation, soon reach their maximum and then decline, the ammonia somewhat faster than the hydrogen sulphide. The cyanogen and carbon disulphide on the other hand gradually increase as the temperature rises.

There seems to be some connection between the proportion of ammonia and cyanogen which has been explained by the probable reaction:

$$NH_3 \left\langle \begin{array}{l} 2CN + 3H_2 \\ N_2 \quad + 3H_2 \end{array} \right.$$

The critical temperatures of maximum yield seem to be about 450–480° C. for ammonia and from 900–950° C. for cyanogen. When the temperature rises above 1000° C. these gases seem to be decomposed into their elements.

The ratio and quantity of hydrogen sulphide and carbon disulphide seems to vary not only with the temperature but also with the method of carbonization as the vertical retorts apparently yield less fixed sulphur compounds than the horizontal retorts and probably more hydrogen sulphide. In general the total sulphur compounds in the gas increase with the sulphur in the coal, but a table below shows how the sulphur is distributed with some American coals when tested in horizontal retorts.

COMPARATIVE COKE ANALYSES

	Bee Hive Ovens.	Retort Coke Ovens.	Vertical Retort.	Horizontal Retort.
Moisture	.35	1.25	1.35	2.57
Volatile compounds	.34	1.61	1.73	3.84
Fixed carbon	92.69	86.66	87.40	86.05
Ash	5.89	10.48	9.52	7.54
Sulphur	.74	.77	.99	.96
Real gravity	1.83	1.90	1.82	1.73
Per cent of coke	52.07	49.49	59.25	53.89
Per cent of cells	47.93	50.51	40.75	46.11

Gas. The gas as it issues from the coal passes out through the mouth-piece and up the ascension pipe, and by means of the dip-pipe enters the hydraulic main. This acts as a seal to prevent the gas escaping from the hydraulic main back into the retort when the mouth-piece is open for charging or discharging. Fig. 228 shows the general plan of coal gas plant.

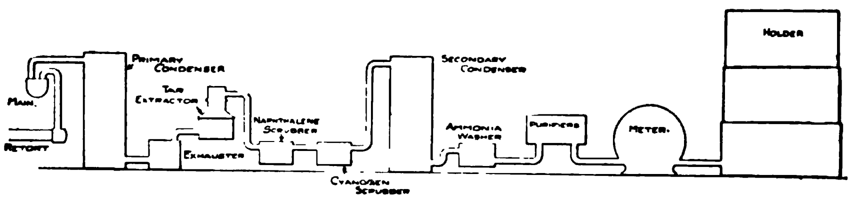

Fig. 228.—Outline of Condensation and Purification of Coal Gas.

Ordinarily, there is an ascension pipe for each retort, but in some cases one ascension pipe serves three retorts, which are set directly above one another. This system is, of course, only applicable where the retorts are charged and discharged simultaneously by machinery.

Hydraulic Main. The desirability of the use of a liquid seal in the hydraulic main is subject to some question, and there are a number of methods proposed and in use whereby this seal may be lowered after the retort has been charged, thus putting the retort in direct connection with the hydraulic main, and then raising it so that the retort is sealed off when the lids are opened for charging and discharging. Valves of different design have also been used for this purpose.[1]

When the hot gases come in contact with the liquid in the hydraulic main, a certain amount of tar is deposited; this is removed automatically from the main in order that it may not come into direct contact with the gas, and thus cause a deterioration of the candle power.

The crude gas leaves the hydraulic main at a temperature of from 65 to 75° C., and contains a number of impurities—tar, ammonia sulphuretted hydrogen, organic sulphur compounds, naphthalene and cyanogen—which must be removed in whole or in part before the gas

[1] Hydraulic Mains: G.W., Dec. 11, 1909, p. 721; A.G.L.J., Nov. 5, 1906, p. 809.

is considered ready for distribution, and, furthermore, the gas must be brought down to the ordinary temperature. The average content of the impurities in the crude coal gas is given below.

IMPURITIES IN CRUDE COAL GAS

Impurity.	Percentage by Volume.	Grams per 100 Cu.Ft.
Hydrogen sulphide........	.4 -1.6	250–1000 sometimes 3000
Ammonia.	.48 -1 26	150–400 occasionally 550
Cyanogen	.05 - .135	25–65
Organic sulphur...........	.0085- .046	12–65

Condensers. As regards the illuminating value of the gas, the most important impurity to be removed is the tar. At the temperature at which the gas leaves the hydraulic main the tar exists principally as a fog, and also as a vapor, which will condense with a lowering of the temperature. The first step then is a reduction of the temperature in the primary condensers. These are illustrated in Fig. 229, and may be operated with either air or water as the cooling agent.[1]

Tar Extractor. On leaving the primary condensers, in which some of the tar is deposited, the gas is passed into some form of tar extractor,

Fig. 229.—Dephlegmating Condenser.

Fig. 230.—Tar Separator.

[1] Tar Removal: London Journal of Gas Lighting, May 30, 1911, p. 602; Nov. 22, 1910, p. 575; Nov. 1, 1910, p. 324; Oct. 13, 1908, p. 139; June 4, 1907, p. 660.

Condensation: Progressive Age, Oct. 1, 1910, p. 869; London Journal of Gas Lighting, June 28, 1910, p. 953; Oct. 25, 1908, p. 58; American Gas Light Journal, Jan. 31, 1910, p. 203.

Naphthalene: J.f.G., May 27, 1911, p. 496; L.J., Aug. 30, 1910, p. 581; L.J., March 15, 1910, p. 723; G.W., Sept. 11, 1909, p. 301; L.J., Sept. 7, 1909, p. 627; G.W., May 8, 1909, p. 624; L.J., March 16, 1909, p. 783.

the usual form being that of the P. & A., which consists, as shown in Fig. 230, of a drum composed of a series of perforated sheets consisting of alternate series of small holes and blanks so arranged that the blank spaces in one set of sheets opposes the perforated sections in the adjoining sheets. Another form of apparatus is known as the washer-scrubber. In this, the gas passes through a number of small openings into contact with ammonia liquor, the action of the water causing the tar particles to coalesce and be condensed. It is found that the most efficient operation for the removal of tar requires a temperature of from 105 to 115° F.

Fig. 231.—Exhauster.

Exhauster. The gas is now passed through the exhauster, Fig. 231, which operates to maintain a constant pressure in the retorts and to furnish the pressure necessary to overcome the resistance of the train of purifying apparatus, and to force the gas into the storage holder.

Scrubber. From the exhauster the gas passes into the naphthalene scrubbers. These scrubbers, Fig. 232, are composed of horizontal cylinders divided by a number of vertical partitions. A central shaft carries a disk made up of a large number of short wooden rods set parallel to the axis of the shaft, and arranged so that as they revolve they dip into the contents of the scrubber, and on rising present a large wetted surface

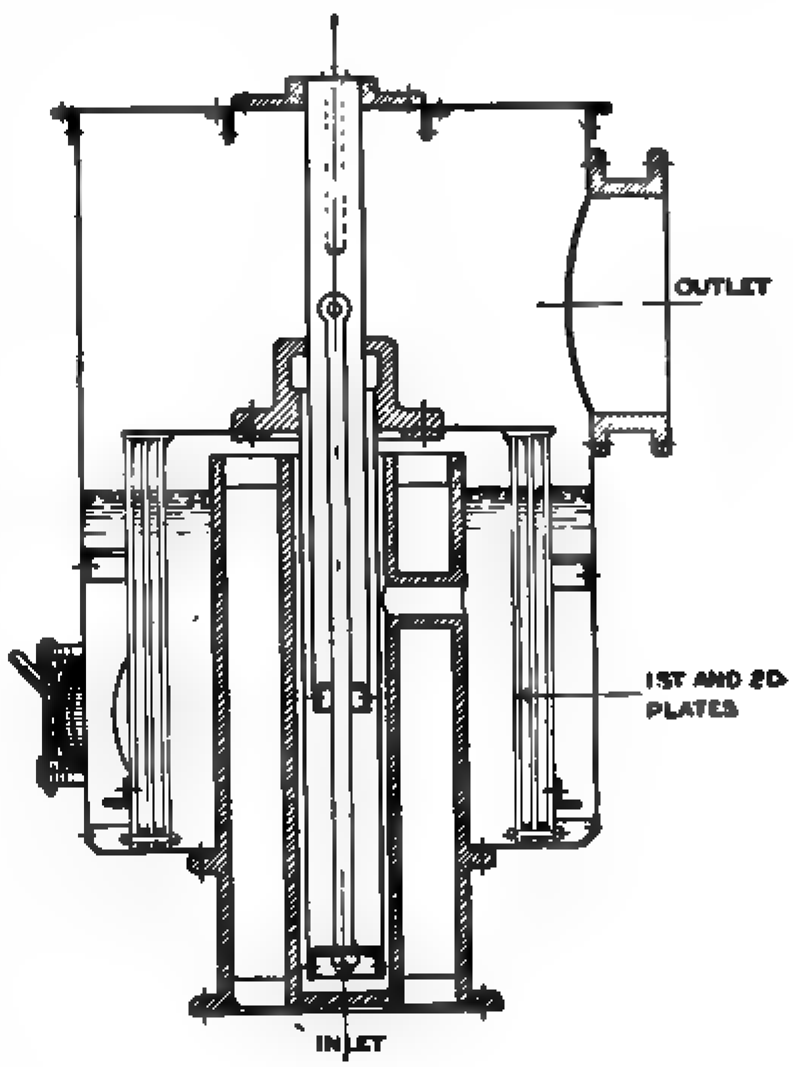

Fig. 232.—P. & A. Tar Extractor.

in contact with the stream of gas. A heavy tar oil, such as anthracene oil, water gas tar or vertical retort tar, is the material generally used for the removal of naphthalene.

FIG. 233.—Thermostat used in securing uniform condensing temperature by automatically regulating the supply of cooling water.

When cyanogen is extracted it is usually removed by means of a washer similar to the naphthalene washer. The solutions used vary according to the processes employed, but they usually consist of an alkaline solution of ferrous sulphate. The gas now passes to the ammonia

FIG. 234.—Rotary Ammonia or Naphthalene Scrubber.

scrubbers, Fig. 234. In order that the absorption of ammonia by water, which is usually used to remove it, will be complete, it is necessary that the temperature of the gas be reduced to about 60°. This reduction in temperature is secured in the secondary condensers; these are always water cooled in order to secure the low final temperature that is necessary.

This absorption was formerly carried on in large towers filled with cobble stones or boards, or other devices exposing a large surface, which was kept moistened by water or weak liquor passing down from the top. This form of scrubber has been generally replaced by the more compact washer-scrubber similar in construction to that described for cyanogen removal. In these mechanical scrubbers the ammonia is completely removed by the use of from 10 to 15 gallons of water per ton of coal carbonized, and as the gas is at the same time brought into contact with the concentrated ammonia liquor at the inlet end of the scrubber, a considerable proportion of sulphuretted hydrogen and carbon dioxide is also removed.

REMOVAL OF IMPURITIES IN CRUDE COAL GAS BY CONDENSATION AND SCRUBBING

	Hydrogen Sulphide Grams per 100 Cu.Ft.	Ammonia. Grams per 100 Cu. Ft.	Carbon Dioxide. Per Cent by Volume.
Outlet of exhauster	610	223.1	2.57
Outlet of condensers	590	196.4	2.34
Outlet of lower scrubbers	470	93.1	1.98
Outlet of rotary scrubbers	400	.37	1.58

Ammonia Liquor. The ammonia liquor and tar that are removed in the different points in the condensing and purifying system are collected and passed through what is known as a separator. In this apparatus, the stream of mixed liquor in passing through the separator is baffled and turned in its course a number of times, so that the tar which has a specific gravity of 1.2, and higher, falls to the bottom and may be removed, while the liquor rises to the top and may be pumped off to the ammonia storage tanks.

A number of processes have been invented for the extraction of the ammonia from the heated gases, and the immediate formation of soluble ammonium salts. Among these are the processes employed by the Otto Hilgenstock Coke Oven Co., the Koppers Process, and the combination purifying and ammonia extraction process of Burkheiser and Feld.

The remaining impurities in the gas are sulphuretted hydrogen and organic sulphur compounds.

Purifiers. The sulphuretted hydrogen is generally removed by passing it through large vessels, called purifiers, Figs. 235 and 236, where it is brought into contact with some form of ferric oxide. There is considerable discussion as to the exact reactions which take place. The probable reactions are

$$Fe_2O_3+3H_2S=Fe_2S_3+3H_2O$$

and

$$Fe_2O_3+3H_2S=Fe_2S+S+3H_2O.$$

It seems likely that these two reactions take place simultaneously, and the proportions of ferric and ferrous sulphide formed are dependent upon the nature of the oxide and the other conditions. It is said to be in the relation of three parts ferric to five parts ferrous sulphide. When the oxide has become saturated it is removed from the purifiers and exposed to the air, where, under the influence of the atmospheric oxygen, ferrous oxide is formed and free sulphur set free.[1]

In order to take advantage of this reaction, small quantities of air are sometimes admitted to the crude gas before entering the purifiers, the oxygen in which reacts with the partially fouled purifying material,

Fig. 235.—Water Sealed Purifier, Shallow Type.

and thus considerably increases the length of time before it is necessary to remove it.

The purifying material is composed of either a natural ferric oxide, or is made by coating shavings or other porous material with rusted iron borings.

In the older type of purifiers the oxide was contained in shallow cast-iron boxes provided with water sealed lids, the oxide being carried on

[1] General: London Journal of Gas Lighting, Sept. 15, 1903, p. 676 et seq.; June 4, 1907, p. 658; Progressive Age, November 15, 1904, p. 584.

Theory: Gas World, Aug 25, 1905, p. 356; Feb. 8, 1908, p. 158; Feb. 15, 1908, p. 198; London Journal of Gas Lighting, Sept. 1, 1908, p. 582; Gas World, April 16, 1910, p. 493.

Removal of CS: Gas World, Aug. 21, 1909, p. 227; Oct. 22, 1910, p. 487.

Special Processes: London Journal of Gas Lighting, Aug. 23, 1904, p. 527 et seq.; Gas World, March 18, 1911, p. 343; London Journal of Gas Lighting, June 28, 1910, p. 959; March 15, 1910, p. 729; Journal des Usines à Gaz., Nov. 5, 1909, p. 326.

wooden trays in two layers of about 30 ins. each. These boxes were arranged usually in sets of four or six, and so connected with valves that the sequence of boxes could be varied at will, and any box could be removed from service for cleaning.

It has now been found more economical to put the oxide into only two or three large boxes, building these either of steel or concrete out of doors, and thus saving expensive buildings.

Widely divergent views are held as to whether it is the time of contact, the velocity of flow, or the total volume of the oxide in use that is the determining factor in calculating the apparatus necessary for the purification of the gas. It is usually estimated, however, that with the use of a slow velocity a certain total volume of purifying material is required.

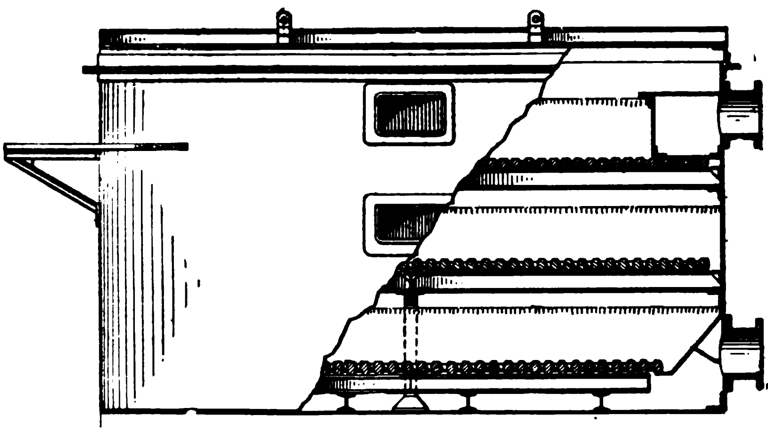

FIG. 236.—Dry-seal Purifier. Deep Cheese-box Type.

The economical volume of oxide and its uses are functions of the capital charges for installation and the cost of changing and revivifying the fouled oxide.

In the older type of purifiers, using a number of boxes of relatively large area, with layers of oxide from 3 to 5 ft. in depth, it was usually assumed that 1 sq.ft. of area in a box would purify about 1500 cu.ft. of coal gas per 24 hours. At present, the tendency is to concentrate the oxide in two or three large circular boxes where the oxide is 10–15 ft. deep. Here the usual allowance is about 300 cu.ft. of gas per cu.ft. of oxide per 24 hours.

In testing the operation of the purifiers, we find that the first box removes the greater portion of the hydrogen sulphide, and that as the percentage of sulphur decreases it becomes increasingly difficult to remove it. The purifiers are usually arranged, therefore, so that at least one box is kept filled with fresh and active oxide to retain slight traces of sulphuretted hydrogen which might pass through the other boxes which remove the bulk of the impurity.

With the repeated revivifications of the oxide, free sulphur accumulates to such a point (40 to 50 per cent) that it mechanically coats the iron, so that the efficiency of the oxide is slightly reduced.

When the cyanogen is not removed it combines with some of the iron, forming Prussian blue; this takes place at the surface, and further reduces the efficiency of the oxide. Some analyses of spent oxide are given showing the approximate content of Prussian blue, sulphur, etc., that may be expected.

ANALYSES OF SPENT PURIFYING MATERIAL

	Coal Gas.	Water Gas.
Times used	12	19
Weight per bus. dry	39.24 lbs.	61.61 lbs.
Original moisture	21.20%	7.31%
Analysis on dried sample		
Ferric oxide	26.71%	36.87%
Metallic iron	.06%	
Free sulphur	54.56%	36.84
Prussian blue	2.56%	
Tar	4.11%	13.54%
Shavings	12.00%	12.75%

When the gas was formerly purified with slaked lime, partially sulphided lime reacted with the organic sulphur compounds, and thus removed a considerable portion of them. With the present almost universal use of iron oxide, however, a much smaller proportion of the organic sulphur is taken out. The small percentage that is removed is undoubtedly due to its solvent action on the free sulphur present in the purifying materials. A number of processes have been proposed for the removal of organic sulphur, but in general they have not proven very successful. Among these processes is the use of aniline in combination with a metallic oxide, clay mixed with the regular purifying material, and the use of mixtures of anthracene oil with certain resinous compounds. In this connection, mention should be made of a process developed for use with the all oil water gas on the Pacific Coast. In this process, the gas is passed through heated checkerbrick, whereby the organic sulphur compounds are broken up, forming hydrogen sulphide, which is then removed by the ordinary form of oxide purification.

Benzol Enrichment. In the ordinary process for the manufacture of coal gas the photogenic value of the gas is sometimes lower than that desired, and in the absence of a carburetted water gas plant, which is the most economical and efficient method of enriching and controlling the candle power of the gas, the most available method for enriching is the addition of benzol vapor.[1]

[1] Benzol Enrichment: P.A.G.I., 1909, p. 91; P.A.G.I., 1908, p. 247; P.A., May 1, 1908, p. 280; P.A., May 15, 1905, p. 232 et seq.

Theoretically, coal gas should be able to carry over 3 per cent of benzol vapors at 32° F.; this would result in a gas of about 30 c. p. Practically, however, this result is not attained. This is due to the varying composition and resulting vapor tensions of the benzol vapor added and of the hydrocarbon vapors already present in the gas. The enriching power of benzol may vary from 13,000 to 38,000 candle feet per gallon; the usual commercial figures are from 20,000 to 24,000. In general, the efficiency of the enrichment decreases as the volume of vapor increases and with the higher initial candle powers.

The most successful results are now attained by scrubbing the gas with a heavy oil, thus removing all condensible constituents, and then re-enriching with a high grade of benzol.

Water Gas. The manufacture of water gas depends upon the decomposition of steam by the action of incandescent carbon. The gas made by this reaction is called " blue gas," and while it has a heating value of about 300 B.T.U. per cubic foot it is non-luminous. In order to render the flame luminous it is necessary to add some hydrocarbon that will liberate free carbon in the flame. Many early patents were taken out to do this, but the process did not become important until the Pennsylvania petroleums became commercially available.

The modern apparatus is the development of the Lowe apparatus that was patented in 1872–1875. In it present form it is a very efficient process, as every feature has been considered both from a theoretical and operative standpoint. The supply of air and steam is metered. The temperatures in the fixing chambers is controlled with electric pyrometers and the sensible heat in the off-going blast and illuminating gases is recovered in greater part in economizer boilers that return sufficient steam to operate the plant.

The apparatus shown in Fig. 237 has a capacity of 1,500,000 cu.ft. per day, but units having a capacity of 3,000,000 cu.ft. per day are in regular operation.

Operation. The operation of a modern plant, Fig. 237, is as follows: The generator is charged with the fuel through the coaling door *A*. After ignition, it is raised to a point of incandescence by a blast of air supplied under a pressure of from 16 to 20 ins. through the blast pipe *B*, passing through the interlocking valve *C*, which is so connected that it will be impossible for the blast and the gas to come together and thus cause explosions. The air passes down through the Venturi meter *D* and is controlled by the valve *E*, where it enters the generator beneath the grate, passing through the fuel bed, where the reaction $C+O_2=CO_2$ and $CO_2+C=2CO$. The temperature of the fuel rises rapidly and a certain amount of producer gas is formed. This passes through the pair of valves *FG*, *F* being open during the blast, through the connection *H*, into the carburetter. The carburetter, which is a fire-brick lined vessel filled with checker-brick, is brought to the required temperature by the sensible

heat in the blast products, and by the combustion of their CO by means of a secondary supply of air entering through the valve *I*. From the carburetter the products pass downward and up through the superheater, out through the valve *K* to the stack. When it is desired, the tertiary supply of air can be admitted through the valve *J* at the base of the superheater, causing further combustion, if desired, and local heating in this part of the apparatus. Fig. 238 shows the working floor of the apparatus.

When the carburetting and superheating vessels have been brought to the proper temperature, fuel in the generator is very highly heated.

FIG. 237.—Modern Lowe Apparatus.

The air blasts are cut off in the order *J*, *I*, and *E*. The stack-valve *K* is closed by means of lever *L*, and steam is introduced by means of the valve *M* and the steam meter *O* beneath the grate. The steam passes up through the bed of incandescent fuel, where the reactions $C+H_2O=H_2+CO$, and the further general water gas reactions $CO+H_2O=CO_2+H_2$ take place. The water gas passes into the carburetter, where it meets the carburetting oil, which is measured by the meter *Q* and is sprayed into the carburetter through *R*. The sensible heat of the water gas and the high temperature in the surface of the checker-bricks vaporize the oil. The mixture of water gas and oil vapors then passes down through the carburetter, where the vaporization is completed, a considerable portion of the vapors decomposed and to some extent polymerized into fixed gases. Passing from the base of the carburetter up through

the superheater, the temperature of the checkerbrick of which is very carefully regulated, the decomposition of the oil vapors is carried to the most advantageous point, and the resulting mixture is composed of fixed gases, some condensible vapors and a small quantity of complex hydrocarbons, known as water gas tar.

Fig. 238.—Operating Floor, Water Gas Plant.

FORMATION OF CARBURETTED WATER GAS

	Top of Generator.	Base of Carburetter.	Middle of Superheater.	Top of Superheater
Illuminants	00	10 75	14 75	14 75
CO	39 75	33 05	30 70	30 65
H_2	50 00	43 05	34 60	31 35
CH_4	2.20	1 10	12.30	16.75
C_2H_4	.00	5 60	1.45	.30
CO_2	4 60	4 00	3 70	3.70
O_2	.35	30	.30	.30
N_2	3 10	2 15	2 20	2 20

These pass out through the connection to the valve K, through the dip-pipe S into the wash-box, which acts as a hydraulic seal and prevents both the escape of the products of combustion during the blasting period and the return of the illuminating gases. In contact with the water in the wash-box, the temperature of the gas is reduced from 1200 or 1300° F. to about 190° by the vaporization of the water, and some of the tar is deposited. The gases pass out of the wash-box through the connection to the base of the scrubber, and rise through the staggered nest of wooden trays, where the entrained solid matter, con-

siderable water, and some tar are deposited by impingement and the temperature is somewhat reduced. From the top of the scrubber it passes into the top of the condenser through the water-cooled tubes. By means of the cooling water the temperature is reduced to 150° F., and it passes out of the connection Z to the relief holder.[1]

Fuel Used. The fuels used in the manufacture of water gas are anthracite and semi-anthracite coals and the various grades of coke. As they are used primarily as a source of carbon they should be high in fixed carbon, containing not over 7 per cent of volatile combustible, as some of this is liable to loss during the blasting period. The ash should be low and of high fusing point so that the formation of clinkers may be reduced to a minimum, although fuels containing as high as 25 per cent of very fusible ash can be utilized successfully. The fuel should be uniform in size to permit the free flow of the blast and steam and it should be low in moisture and sulphur. A table of typical analyses of the different classes of fuel used in the manufacture of water gas is given with the analyses and fusing points of the ash of some American coals.

COMMERCIAL ANTHRACITES

	Moisture.	Vol. Amt.	Fixed Carbon.	Ash.	Sulphur.	Color of Ash.
Buck Mountain	3.08	5.22	80.56	11.14	.93	Reddish tan
Lackawanna	2.80	7.61	78.71	10.88	.74	Gray
Lehigh	2.97	5.35	81.59	10.09	.73	Yellow gray
Pittston	1.93	8.60	77.20	12.27	1.10	Gray
Susquehanna	2.75	7.45	80.20	9.61	.71	Lt. gray

COMPOSITION OF ASH AND FUSING POINT

Ash in Coal.	7.67	4.80	5.49	4.02	8.93	5,40	5.18
SiO_0	41.94	42.17	46.55	39.00	49.99	36.80	49.03
Al_2O_3	24.04	35.58	35.68	26.21	31.97	31.25	41.98
CaO	11.08	4.76	5.00	3.97	2.13	2.80	1.79
MgO	1.28	....	1.00	.67	.81	tr.	tr.
Fe_2O_3	14.56	12.70	7.80	21.95	12.23	21.95	5.02
SO_3	4.61	3.21	3.76	4.44	.26	2.76	1.86
Alkalies and undet.	.49	1.68	.21	3.76	2.61	4.44	.32
Color of ash	Terra cotta	Terra cotta	Lt. gray	.....	.....	Lt. gray	Lt. gray
Fusing point, ° F.	2147°	2280°	2350°	2390°	2570°	2640°	3020°

[1] Theory: Bulletin of Mines, No. 7, 1911; Engineering, May 5, 1911, p. 601; P.C.S., 1910, p. 2178; J.f.G., 1909, 52, p. 282; Z.f.A.C., 1906, vol. 50, p. 276; J.f.A.C., vol. 48, p. 735; J.f.A.C., 1905, vol. 44, p. 267; Thermodynamik Chemiker Gas Reaktion, Haber, p. 254; J.f.G., 1904, vol. 47, p. 268; J.f.Elek., 1903, vol. 9, p. 691; B. 1903, 36, p. 1231; J.f.G., (1900), 43, p. 355 et seq.; C.R. (1900), 131 p. 1204; C.R. (1900), 130, p. 132; C.R. (1899), 128, p. 824, p. 1524; J. f. phy. C., 44, p. 510; 48, p. 735. Lehrbuch der chemischen Technologie der Energien, H. v. Japtner.

Operation: A.G.L.J., May 15, 1911; P.A.G.I., 1910, p. 215; L.J., March 1, 1910, p. 581; A.G.L.J., April 18, 1910, p. 730; L.J., Jan. 18, 1910, p. 173; P.A., April 15, 1909, p. 329; P.A., May 15, 1907, p. 266.

Enriching Oils. The oils available for enriching purposes vary in their composition in the different fields. The oils from the Pennsylvania, Ohio, Indiana, and Illinois are composed principally of the paraffine and olefine series; the oils from Kansas and Indian Territory differ somewhat according to their gravity, the lighter oils containing considerable paraffine while the heavier oils contain some paraffines but principally naphthenes. The Texas oils contain almost no paraffine, but contain a considerable proportion of complex hydrogenated ring compounds; they are made up of members of the C_nH_{2n-2} and C_nH_{2n-4} series. The California oils are made up almost entirely of complex ring compounds. The Louisiana oils vary with their gravity, some resembling Texas and others the California oils.

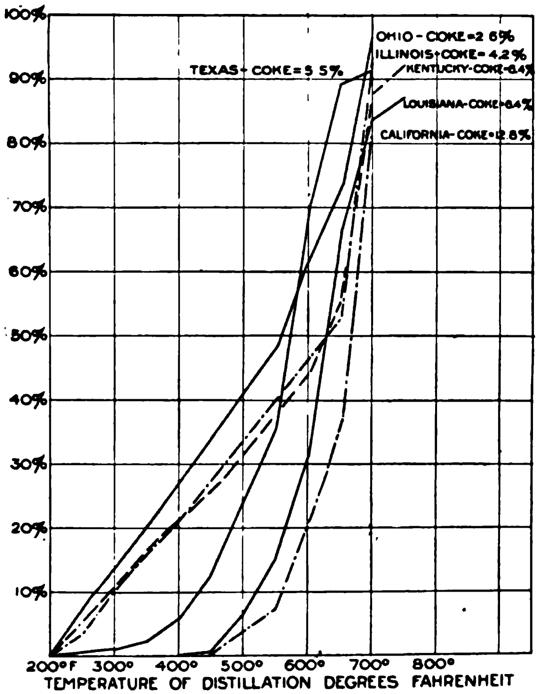

FIG. 239.

As enriching agents it seems that the paraffines are the most valuable, the presence of double carbon linkages and rings reducing the efficiency. Where ring compounds are present, however, the more fully hydrogenated are the more valuable. Benzenated ring compounds are almost valueless.

The yield of tar on gasification is an indication of the presence or absence of complex hydrocarbons in the oil. In the oils from Pennsylvania it will run from 8–10 per cent of the oil, while the Texas and California oils will yield from 15–18 per cent, denoting the presence of complex ring and asphaltic compounds.

COMPARATIVE YIELD OF WATER GAS TAR FROM DIFFERENT OILS

Naphthas,	paraffine base,	2–4	per cent by volume of oil.
Gas oils,	paraffine base,	6–10	" " "
Crude oils,	paraffine base,	8–12	" " "
Gas oils,	asphaltic base,	10–15	" " "
Crude oils,	asphaltic base,	12–18	" " "

COMPARATIVE DISTILLATIONS OF WATER GAS TARS FROM DIFFERENT OILS

Crude Products

Fractions.	Per cent by Wt.	Gravity.	Per cent by Wt.	Gravity.	Per cent by Wt.	Gravity.
Light oils	.31	.8850	3.46	.8811	5.55	.8898
Middle oils	16.86	.9885	31.25	.9972	30.63	1.0030
Anthracene oils	49.34	1.0801	46.68	1.0887	43.17	1.0973
Residuum	33.42	....	19.02	....	20.35	
Fractionation of the Light Oils						
200–250° F.	.00	....	.80	.8758	1.61	.8826
250–300°	.27	....	1.53	.8807	1.95	.8860
300–350°	.04	.8850	1.13	.8856	1.99	.9044
Original Material						
Specific gravity at 60°.	....	1.1427	....	1.0881	....	1.0902
Free carbon	.21	....	.02	....	.06	

The reactions involved in the formation of oil gas are almost identical with those occurring during the latter stage of the carbonizing of coal in a retort, the principal difference being that in this case the oils vaporize readily and the temperature is under more exact control.[1]

The products formed with increasing temperatures seem to follow in general the reactions that were discussed under the distillation of coal; the illuminants decrease and the hydrogen increases while the paraffines remain about stationary.

EFFECT OF TEMPERATURE ON DECOMPOSITION OF OIL

Temperature. C.	Gas per Gal. Cu.Ft.	Tar. Per cent.	Coke. Per cent.	Olefines. Per cent.	Paraffines. Per cent.	Hydrogen Per cent.
711	56.4	28.0	1.83	38.0	48.0	11.1
741	61.5	29.4	2.43	33.8	48.3	14.1
751	63.7	26.2	3.63	31.3	50.3	13.5
789	68.0	24.2	3.45	25.0	49.2	19.1
832	80.3	11.9	12.43	13.1	47.0	33.6

The influence of the high partial pressure of the hydrogen is especially marked in the formation of carburetted water gas as the blue gas contains nearly 50 per cent of hydrogen. The hydrogen inhibits the decomposition of the primary products and the splitting off of more hydrogen, which unites with the complex residues resulting in a higher percentage

[1] Fuel: A.G.L.J., June 14, 1909, p. 1073.

Oils: P.A., June 1, 1909, p. 435; A.G.L.J., Sept. 20, 1909, p. 725.

Decomposition of Oils: J.f.G., Jan. 15, 1910, p. 53 et seq.; Z.f.A.C., 1908, p. 602; A., 1907, 32, p. 241; J.f.G., 1908, p. 265; J.f.G., 1907, p. 45; C.Z., 1899, p. 916; B.B., 1896, p. 552; J.f.G., 1898, p. 221; J.S.C.I., 1884, p. 462.

of olifines, somewhat less gas and more tar. The following table shows the composition of oil gas at a given temperature, and the calculated and observed mixtures of oil and blue gas:

CALCULATED AND OBSERVED COMPOSITION OF CARBURETTED WATER GAS

	Blue Gas.	Oil Gas.	Calc. Carb. W. G.	Obs. Carb. W. G.
Illuminants........	.0	36.6	9.5	14.8
CO...............	39.8	1.1	29.7	30.6
H_2...............	50.0	13.3	40.5	31.4
OH_4..............	2.2	40.4	12.1	16.8
C_2H_6.............	.0	6.9	1.8	.3
CO_2..............	4.6	.5	3.5	3.7
O_2...............	.4	....	.3	.3
N_2...............	3.1	1.3	2.6	2.2

This shows the increased illuminants and decreased hydrogen and increased tar. It should be noted also that in practical operation we obtain about 6000 candle feet per gallon of oil in carburetting water gas while we should only obtain about 3000 candle feet if the oil gas were used alone.

In determining the practical enriching value of an oil it is run in a machine for some time with different temperatures in the fixing chambers and the candle feet per gallon calculated and plotted against the temperature. The maximum value and its corresponding temperature is then easily determined. A typical curve of this kind is reproduced below, Fig. 240.

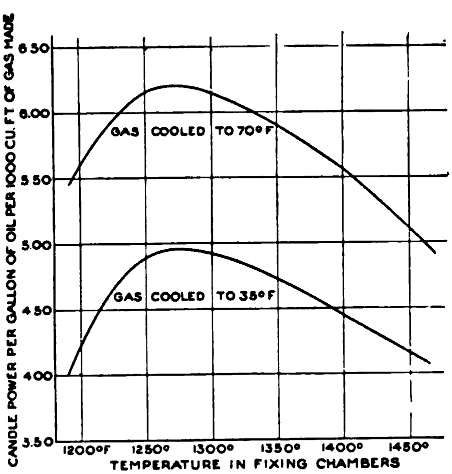

Fig. 240.

In considering the theory of the formation of the blue gas or water gas proper we have the two general steps—storing heat in the fuel bed by the combustion of a portion of the fuel with a blast of air, and utilizing this heat in decomposing steam with the formation of the water gas which is an endothermic reaction.

During the blasting period the primary reaction is probably:

$$C+O_2=CO_2 \quad \text{or} \quad 2C+O_2=2CO.$$

These equations are connected by relation $CO_2+C=2CO$, which is the equation for the equilibrium. Clement and Haskins have

given the following expression for the value of K at any temperature, viz.:

$$K = \frac{C_{(CO)}}{C_{(CO)}}.$$

$$\text{cn}K = -\frac{20235}{\theta} + 1.035\text{cn}\theta - .001564\theta + 8.604,$$

and they found that with coke the following percentages were in equilibrium at different temperatures:

Temperature.	Carbon Monoxide.	Carbon Dioxide.
900	83.2	16 8
1000	94.5	5 5
1100	98 1	1.9
1200	99.4	.6
1300	99.7	.3

It must be remembered, however, that in commercial producer gas the presence of the nitrogen lowers the partial pressure of the carbon monoxide, and thus slightly increases the ratio $CO \div CO_2$ over that given in the table. It is found that the time of contact is very important, and that with the increasing temperatures the increase in the coefficient

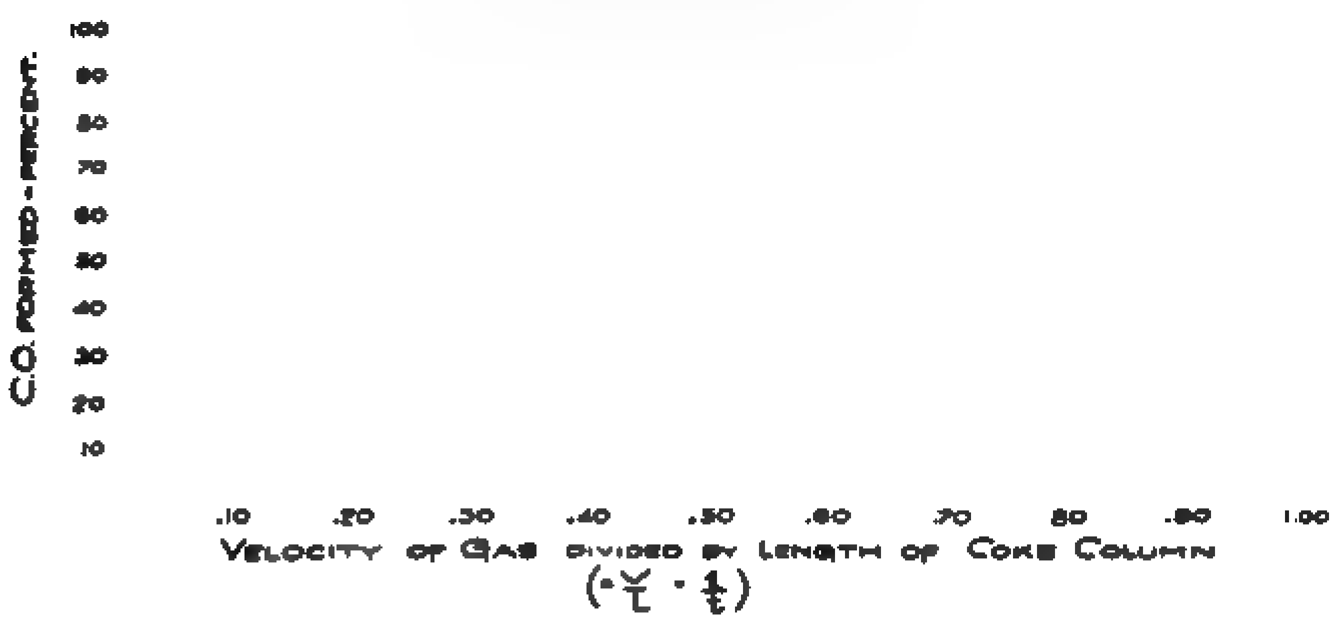

FIG. 241.

of the reaction velocity is about ten times the increase in the diffusion constants, so that velocity of the chemical combination is the determining factor in this reaction

It is found that the differen forms of carbon react differently, charcoal reacting most rapidly, coke next, and anthracite most slowly. In the second stage of the process, that of the decomposition of steam, we have two reactions: $C + H_2O = CO + H_2$, and $C + 2H_2O = CO_2 + 2H_2$.

These products are then related according to the two reactions $CO_2+H_2=CO+H_2O$, and by the reaction previously discussed, $CO_2+C=2CO$. The calculation of the constants of the water gas reaction is complicated by the uncertainty regarding the specific heat of the reacting bodies at high temperatures. Haber gives the following equation for the value of K at equilibrium at temperatures or from 685° to 1480° C.

$$\mathrm{cn}K=-\frac{2232}{\theta}-.08463\mathrm{cn}\theta-.0002203\theta+2.4943.$$

From experimental work that has been done on this problem, it is apparent that while the water gas reaction ceases to readjust itself to changes of temperature at about 1400° C. in the Bunsen burner, yet in the water gas generator it seems to adjust itself down to very moderate temperatures. This is probably due to the influence of the ash on the surface of the coal. It is also assumed that in the generator while the gases may be in equilibrium with themselves, they are not in equilibrium with the carbon in the fuel bed. In Fig. 241 are given some experimental results obtained by Clement and Haskins, using coke as fuel, with the time of contact of the steam equal to two seconds.

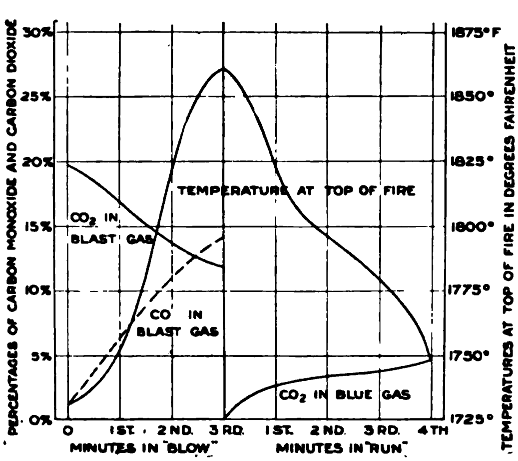

FIG. 242.

In the practical operation of water gas apparatus the efficiency of the production of blue gas will be dependent upon the temperature of the blast gas and water gas issuing from the fire; the percentage of CO or excess air in this blast gas, and the percentage of undecomposed steam in the blue gas, assuming, of course, that we are operating the generator so as to produce a reasonably low percentage of CO_2. These conditions will probably be influenced by the rate and time of passage of blast through the fire. There are two divergent views on this subject. According to one writer, when the rate of passage of blast is sufficiently great in proportion to the depth of fuel, CO will not be formed, but only CO_2. Another writer, on the other hand, finds very little change due to the rate of passage of the gas, and believes that the efficiency of the blow is dependent on the temperature of the fire, and is principally a function of the length of time.

Apparently, an increase in the rate of blast, Fig. 241, will give a higher average temperature of the fire, which results in somewhat increased temperature of the issuing blast gases, with slight decrease in the percentage of CO. It is quite conceivable, in view of the theory that the speed of the reaction $CO_2+C=2CO$, will increase so rapidly with increase in temperature that we cannot sufficiently decrease the time of contact to prevent the formation of considerable quantities of CO.

Increasing the rate of passage of steam will apparently reduce the temperature of the outgoing water gas, which is favorable to economy,

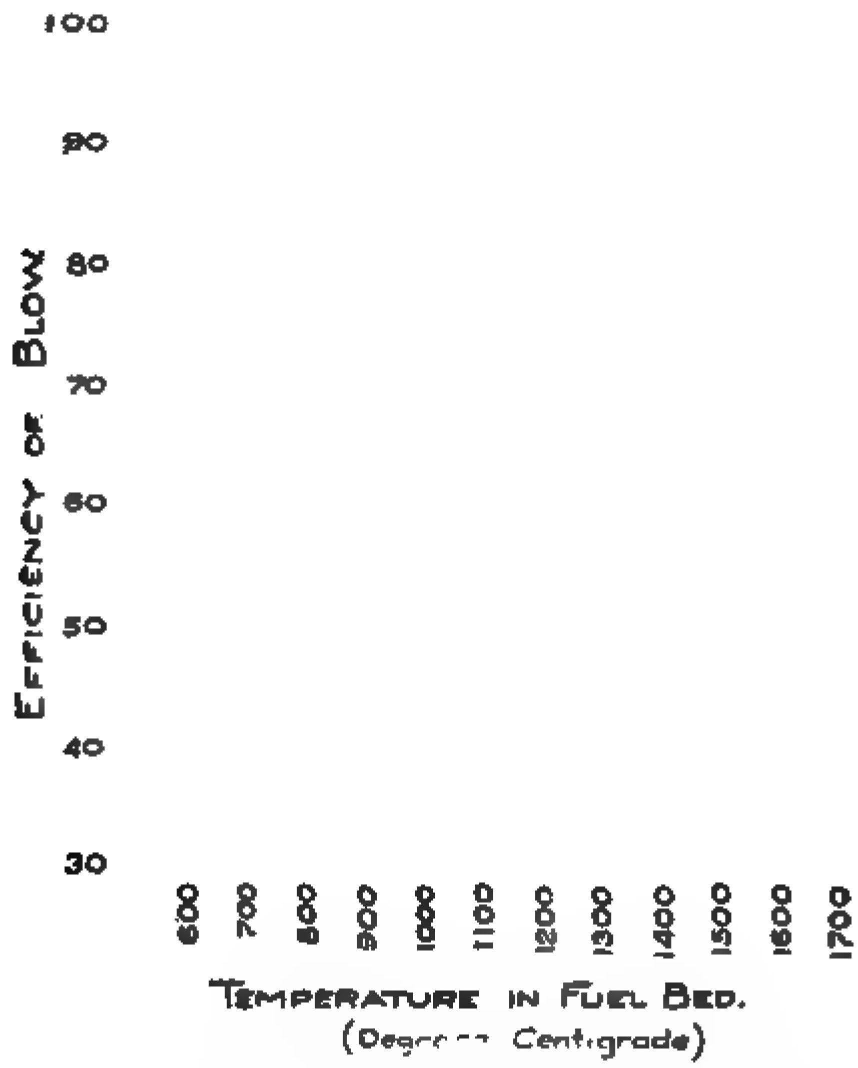

Fig. 243

but this is more than offset by the smaller percentages of steam decomposed, and the consequent waste of both excess steam and its sensible heat, and furthermore, by the greater percentage of CO_2 in the blue gas. In general, all of the writers assume the importance of the slow rate of passage of the steam.

The temperature of the generator fire, Fig. 244, appears to be the most important condition. The capacity of the fuel bed increases with an increase in the temperature, resulting in a larger yield and a more perfect decomposition of the steam, and a more favorable composition of the blue gas. On the other hand it increases the sensible heat of the offgoing blast products and the blue gas, and results in an increased percentage of CO in the blast products, both of which are unfavorable to fuel economy.

The necessity of producing a certain amount of available combustible

in the blast gases to maintain the fixing chambers at the proper temperature somewhat complicates the operation when carburetted water gas is manufactured. With indifferent control of the operating conditions a large excess of CO is always produced with some fuels.

Modern practice attempts to bring the whole fuel bed to a uniform temperature and to reduce the variation or range of temperatures as far as possible, thus enabling the temperature in the active zone in the fuel bed to be maintained at a point where the clinker can be controlled. This results in a minimum loss of sensible heat incurred by the offgoing gases and yet a satisfactory decomposition of the steam is secured at an increased rate.

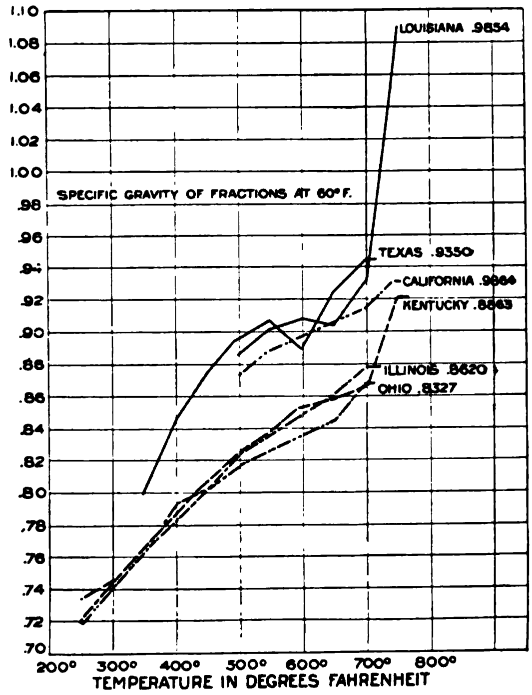

FIG. 244.

The use of two generators that are blasted in parallel but are connected in series, during the gas-making period, is an endeavor to secure more uniform fire conditions.

From the theory of the reactions underlying the combustion of the coal and the formation of water gas, it will be seen that many of the requirements are contradictory. It is therefore necessary to arrange our operating conditions so as to secure the most efficient compromise, remembering that many of the theoretical processes will yield very efficient results under test conditions, but will utterly fail to satisfy the commercial requirements as to overhead charges for capital invested and the labor cost of operating.

The following table gives a set of operating conditions that were in one case found to yield satisfactory results.

OPERATING CONDITIONS

Size of set	8 ft. 6 in.
Area of grate	33.2 sq.ft.
Fuel used, oven coke	
Oil used, Lima gas oil	
Candle-power of gas made	25.2 at 70° F.
Candle-power per gallon of oil	6 at 70° F.
Carbon in generator per M	25 lbs.
Temperature base of superheater	1461° F.
Temperature top of superheater	1300° F.
Length of blow	3 min.
Pressure of blast	20 ins. water
Rate of blast cu.ft. per sq.ft. grate per minute	129 cu.ft.
Generator air used per M. cu.ft. of gas made	1520 cu.ft.
Carburetter air	800 cu.ft.
Length of run	4 min.
Per cent up runs	64.8
Per cent down runs	35
Rate of steam pounds per sq.ft. grate per min	2.1 lbs.
Steam used per M. cu.ft. of gas made	33 lbs.
Gas made per sq.ft. grate per hour	1.910 cu.ft.

The condensation and purification of carburetted water gas differs somewhat from that of coal gas, in that the water gas is more fully saturated with hydrocarbons which must be preserved and retained in the gas to secure its proper illuminating value.

The greatest care must be taken in regard to the temperatures employed throughout the condensing and purifying system to avoid suddenly shocking the gas, and we endeavor as far as possible to keep the gas closely in equilibrium with the surrounding condensate. The gas leaving the wash-box at a temperature of about 190° F. passes through the scrubbers and primary condensers into the relief holder. The bulk of the tar will now have been deposited. From the relief holder it is drawn by means of the exhausters, and pumped through the secondary condensers and tar extractors, which are usually of the P. & A. type described under coal gas, into the purifying house. In case the P. & A. type of extractor is not used, vessels filled with shavings are used to mechanically filter out the entrained liquids.

The purification of water gas is carried on under the same general conditions as those surrounding the purification of coal gas, except that it is desirable to keep the temperature at purifiers above 100°C, and this temperature should be held as uniformly as possible. This is to prevent the gas changing suddenly in temperature, and thus getting out of equilibrium with the purifier material, which is saturated with condensate.[1]

[1] Purification and Condensation of Water Gas: Proceedings American Gas Institute, 1906, p. 593; 1912; 1910, p. 704; Progressive Age, July 16, 1906, p. 447.

The following range of temperatures is an example of conditions which justify the conclusion that the gas is being properly handled:

Temperature of the atmosphere	66° F.
Top of superheater	1200
Outlet of wash-box	190
Inlet of scrubber	180
" relief holder	154
" exhauster	115
" tar extractor	113
" purifier	103
Outlet of purifier	85
" station meter	85

Fig. 245 represents a modern small water gas plant. Figs. 246 and 247 show a line drawing and actual photograph of economiser boilers attached to carburetted water gas plant.

All Oil Water Gas. Directly related to the manufacture of carburetted water gas is the so-called all oil water gas which is used so extensively on the Pacific Coast where there is an abundant supply of cheap fuel oil.

The general theory of this process is that of the pyrodecomposition and polymerization of the oil hydrocarbons as in the Pintsch process, and to some extent carburetted water gas.

In the present form of apparatus which is illustrated in Fig. 248, there are two fire-brick lined shells in the form of a U, with one leg longer than the other, the shorter leg serving as the primary generator while the longer leg serves as a superheater. Both shells are filled with checker-brick. The gas take-off for the blast gases is at the top of the longer leg while the illuminating gas take-off is in the middle.

In the operation of the set, oil and steam are blown into the top of the primary generator while the blast is admitted in the center. The blast is turned on for about three minutes before the oil at a pressure of about nine inches, at the end of this time the oil is turned on at a pressure of about 8 lbs., the atomizing steam at 35 lbs. The heating period is about twelve minutes; at the end of this time the blast is cut off, the valve opened connecting with the wash-box, and the gas-making oil is injected as before, with steam, through another set of nozzles. The gas-making nozzles are located both in the primary generator and also in the top of the secondary generator, so that the flow of oil through the machine can be regulated according to the heat carried in the checker work in all parts of the set. The oil is admitted to the top of the primary generator at first quite rapidly, it is then gradually reduced during the run until at the eighth minute it is flowing at about one-third the initial rate per minute. The oil is admitted to the secondary generator at a slightly slower rate and is gradually reduced in the same proportion. The last two minutes of the run the oil is cut off and the

steam pressure is raised to 100 lbs., and allowed to remain at this pressure for two minutes in order to purge the machine.[1]

The heats in the machine are controlled by the appearance of the overflow from the wash-box, the presence of tar showing that the heat is too low while lampblack from the overflow in the first scrubber shows that the heat was too high. The make of gas per minute during the

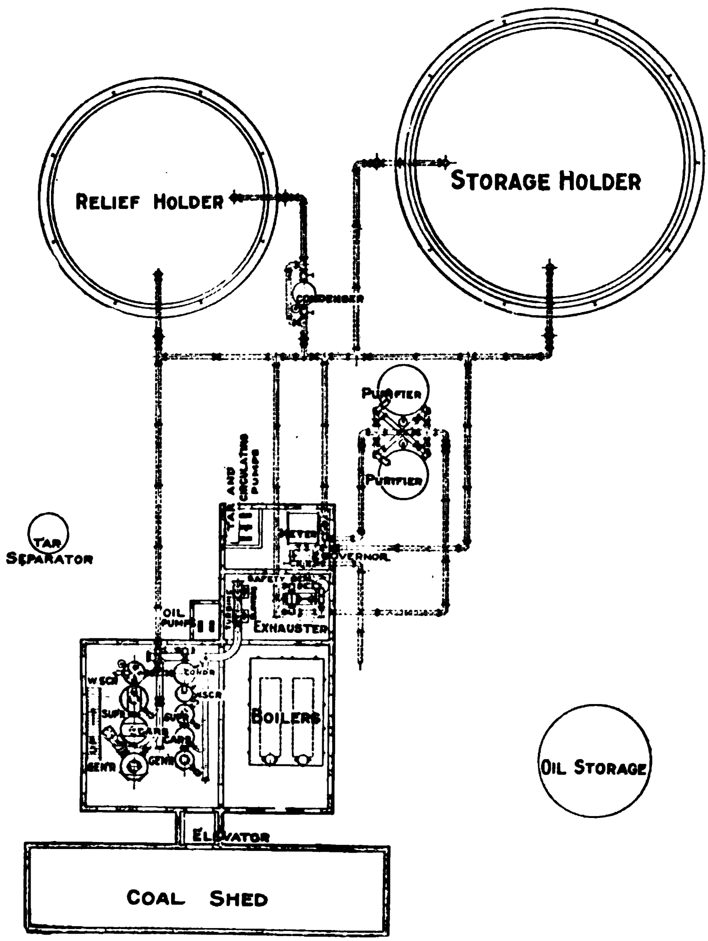

Fig. 245.

run is a very good indication of the heats carried and is an index to the proper length of the run.

In the larger machines about 16 per cent of the total oil used is burned during the heating run so that where the total oil per thousand runs about $8\frac{6}{10}$ gallons, about $1\frac{4}{10}$ gallons per thousand are used during the heating run and $7\frac{2}{10}$ gallons during the gas making run.

[1] P.A.G.I., 1909, p. 410; G.W., May 9, 1908, p. 579; A.G.L.J., Oct. 5, 1908, p. 578.

An average analysis of the oil gas made with a heavy California crude is as follows:

Ills	7.01
CO	9.21
H_2	39.78
CH_4	34.64
CO_2	2.62
O	.16
N	6.58
C. P.	19.69
B.T.U.	680
Sp.gr.	.482

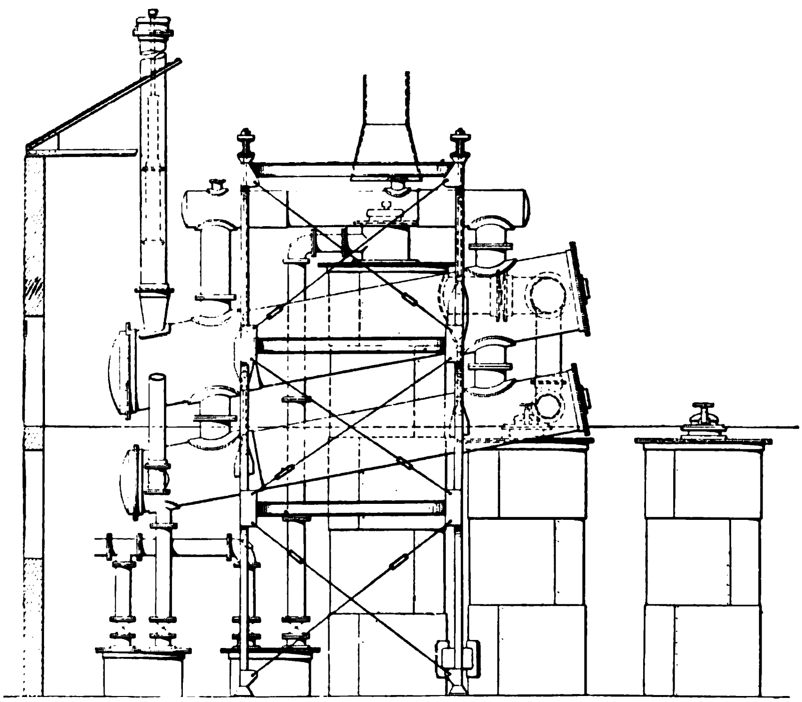

FIG. 246.

In general this gas resembles coal gas in many of its constituents much more closely than it does water gas. But there is every reason why this should be so as both of these gases are formed by the pyrocondensation of hydrocarbons.

The formation of the all oil water gas being almost identical with the second and third stages of the coal gas distillation except that in the case of the oil gas the temperature conditions and time of contact are under much more exact control. In general all that has been said

previously in reference to the decomposition of the hydrocarbons applies with equal force in manufacture of the oil gas in this apparatus.

Fig. 247.

Fig. 248.—Jones' All Oil Water Gas Apparatus.

In the early days of this process the working conditions were not well understood and the operation of the machines resulted in enormous accumulation of lampblack from excessive and irregular temperatures carried in the apparatus. Now, however, with the control that is

exercised over the operation of the set and in addition the better design, the apparatus has resulted in an almost total elimination of the trouble and nuisance due to lampblack. The bulk of the lampblack is now removed in a self-cleaning wash-box in which the lampblack is washed from the gas by a large quantity of water, which prevents the formation of large lumps.

From the wash-box the gas passes through scrubbers filled with wooden trays similar to those used in the carburetted water gas apparatus; as there are no by-products to be saved a rather excessive amount of water is supplied to the scrubbers. In some of the plants three scrubbers are used applying from 10 to 15 gallons per thousand per scrubber, or a total of say 40 gallons per thousand. The water from the wash-box and scrubbers is run into the lampblack separator where the lampblack is removed. The lampblack as taken from the separator contains about 60 per cent of water. This is piled in heaps and allowed to drain until it contains about 20 per cent, it is then used for fuel either under the boilers or in water gas apparatus. In the larger sets about 20 lbs. of lampblack are made per thousand feet of gas.

A great advantage of this type of apparatus is that it can be built and handled in large units, so that the operative labor is reduced to a minimum and from the fact that no time is lost in clinkering. The machines can be depended upon to produce their gas continually so that only a very low holder capacity is required.

Of the available oils in California, it has been found that those highest in gravity give the best results, or in other words, that the hydrocarbons present in the oil are all about equally valuable, so that the oil yielding the greatest weight per gallon will naturally give the greatest number of cubic feet of gas. This result rather bears out the idea that has been gaining ground in the East where the heavier grades of enriching oil have been tried out and experimented with more thoroughly. The sulphur content of the California oils varies quite widely, ranging from a fraction of a per cent to above 4 per cent. It has been found that where the sulphur does not exceed one per cent the gas is easily purified with iron oxide in simple purifiers.

Pintsch Gas. Another commercial adaptation of oil gas is that known as Pintsch gas. Pintsch gas is simply an oil gas compressed to about ten atmospheres and was developed originally for the lighting of railway passenger cars. The Pintsch patents were taken out about 1870.

In this system the oil is first decomposed in a double iron retort, set in a regular coal gas bench, an outline sketch of which is shown in Figs. 249 and 250. The oil is introduced at the front of the upper retort and falls upon a movable tray, which collects most of the carbon formed. The gas and vapors thus produced pass to the back of the upper retort down and out through the lower retort to a hydraulic

main located in front of the bench. The crude gas is passed through a dry scrubber, condenser and purifier and after metering is collected in a low pressure holder, very similar in all respects to the processes employed in condensing and purifying coal gas. The gas is then compressed, generally in a two-stage compressor, into the storage cylinders. Every precaution is taken to remove the condensation thrown down by the compression, so that the gas in the cylinders will be thoroughly

Fig. 249.—Pintsch Retort Bench.

dry. The pressures employed vary from 10 to 14 atmospheres, the latter figure being common in the United States. In some plants, fireclay retorts are employed; in these the oil is passed through the back of the retort and is taken off at the front, so that a single retort suffices. The ordinary form of carburetted water gas apparatus has been used also in the manufacture of Pintsch gas. After the regular blow, instead of turning on the usual supply of steam, only a very small supply is used, just sufficient to clear the machine of the oil gas made. The success

of this work has resulted in the adaptation of a special form of apparatus for generating the Pintsch gas, very similar to the apparatus employed in California for the manufacture of oil gas. In this case, however, the fuel used in the heating run is a tar obtained as a by-product. This is injected into the top of the generator with steam and air until the proper temperature is acquired, then gas oil under pressure is injected, the vapors formed pass down through the heated checker-brick, and are subjected to the same transformations that occur in the water gas set. The heating period is about five minutes, the gas-making period from 6 to 8 minutes. About 1500 cu.ft. of gas are made per run.

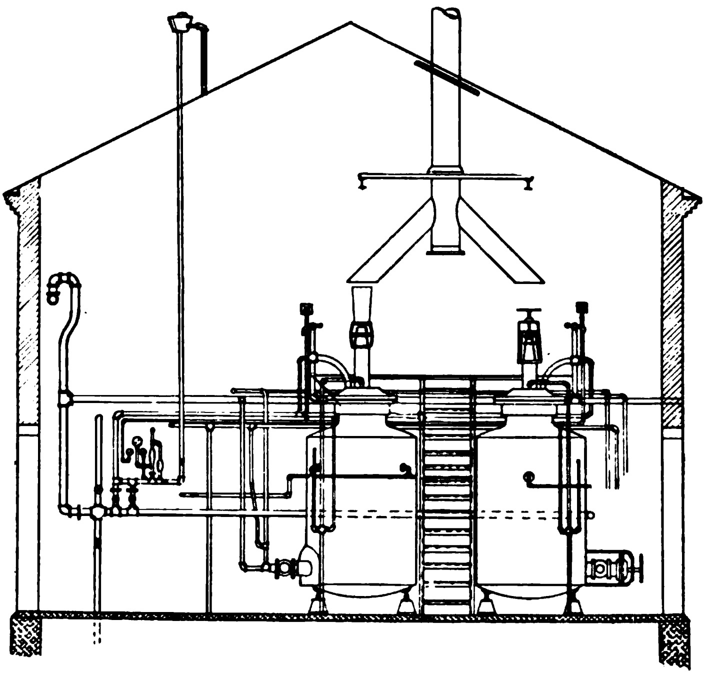

FIG. 250.—Pintsch High Pressure Plant.

It has been found that the candle power is increased by about 10 per cent over that obtained in the retort form of apparatus. A late development of the system is a generation of the gas at high pressure, in a generator built of heavy steel plates, so that the whole operation takes place at high pressure. A small amount of steam in this type of apparatus is injected with the oil. The steam acts as a carrier but does not react with the oil or carbon formed, as the temperature, about 670°, is too low for the reaction to take place. A mixture of gas, tar and water is charged into the store holder at a pressure of about 14 atmospheres. It is purified under pressure and then stored directly into the cylinders. The average composition of the compressed gas is as follows:

Methane	50 to 60 per cent
Illuminants	30 to 40 "
Carbon monoxide	.5 "
Hydrogen	3 to 5 "
Sp. gr. from	78 to .85

The candle power of the gas when tested in open flat flame burners, does not do the gas justice, as it only averages about 40.

The design of the Pintsch regulator and its perfect operation under severe conditions has contributed very greatly to the successful application of the Pintsch system.

At present in addition to its use in railroad lighting, it is extensively employed in buoy lighting. The gas under a pressure of 100 atmospheres is compressed in cylinders which form the body of the buoy. On one gas charge these buoys were run to 528 days. These buoys can be provided with automatic mechanism so that the light can be operated either as a continuous light or in any desired sequence or flashes.

Blau Gas. Another modification of the Pintsch gas is known as Blau gas. In this process the oil is decomposed in the retorts, as in the manufacture of Pintsch gas. The gas is purified and then compressed to 100 atmospheres, so that the greater portion of it liquefies. Under this pressure the liquefied hydrocarbons probably absorb and hold in solution some of the olefines and paraffines that would normally be gases at this pressure. The oil is gasified at a rather lower temperature than that ordinarily employed in the manufacture of oil gas. The fixed gases that are left after compression are used in operating the machinery necessary in the manufacturing operations. The liquefied gas has a specific gravity referred to water of .59. The liquid is sold ordinarily in seamless steel flasks that hold 45 and 10 k.g. The gas is first expanded from 100 atmospheres down to about 10, and is then expanded again to 10 or 12 ins. water pressure. One gallon of the liquefied gas will yield about 28 cu.ft. of expanded gas. There will remain, however, a residue that may run up to 9 per cent. The following may be taken as a typical analysis of the expanded gas:

Illuminants	51.9
CO	.1
H_2	2.7
Methane and ethane	44.1
CO_2	.0
O_2	.0
Nitrogen	1.2
Specific gravity	1.02
Heating value	1704 B.T.U.'s.
Flat flame, calculated at 5 ft. per hr.	48.25

It will be noted that this gas is slightly higher in illuminants and heating value than the Pintsch gas, and is, therefore, slightly more concentrated. It has found some application for use in isolated localities and marine lighting.[1]

Gasoline Gas. Gasoline gas is a mixture of atmospheric air and light hydrocarbon vapor in varied percentages generally above the explosive limit. This gas has been developed to meet the requirements of isolated localities where the quantity of gas required is small, so that the installation of the usual form of coal or water gas apparatus would not be profitable. There are two general systems used in its manufacture; one system operates in the cold while the other system employs heat to aid in the vaporization. Gasoline or carburetted air gas differs from the ordinary forms of coal gas, water gas or oil gas due to the fact that it is a simple mixture of the vapors of a liquid hydrocarbon which is not changed chemically in the vaporization. In the cold process where the air is not heated, a very light grade of gasoline must be employed, while in the system employing steam or other source of heat to assist in the evaporation the less expensive naphthas may be used.

It is essential in either process that the hydrocarbon should be entirely vaporized and should contain no traces of tar which would otherwise stop up the apparatus and give trouble in the burners. The gasoline with a sp. gr. of about .65 is usually employed in the cold system. While this leaves a small residue it is not sufficient to cause serious trouble.

The volume of vapor that can be carried by a given volume of air depends upon the temperature and rises very rapidly with increase in temperature. The data relating to this point are rather meager and frequently somewhat contradictory, but in general, the air can be depended upon to carry over 10 per cent of the vapor, even at low temperatures.

The percentage carried is important in that it must either be lower than the explosive limit, that is less than about 2 per cent, or higher, that is above 5 per cent. In this country, the usual practice is to produce a mixture containing over 5 per cent of the gasoline vapor. The mixtures averaging from 5½ to 6 gallons of gasoline per thousand feet of the mixture. This would give a gas containing over 13 per cent of vapor, which is amply safe from explosion and which would give about 16 candle power in the Argand burner and will have a calorific value about 570 B.T.U's. It can therefore be employed for either lighting or heating.

During the last few years a number of systems have been exploited, using heat to assist in the vaporization of the heavier grades of naphtha. These naphthas have a gravity of from .69 to .71. These machines either use steam or a small flame fed from the machine itself. They

[1] Blau Gas: E.W., June 9, 1910, p. 1516; L.J., June 23, 1908, p. 842.

are generally provided with automatic devices so that their operation is very simple.

The great disadvantage of these systems is the fact that the gas has a high sp. gr., about 1.26, so that in case of leak it does not rise and is thus less readily dissipated by the ordinary means of ventilation. The pipes that are used to convey it are generally of large diameter and care must be taken to prevent exposure to cold draughts, as the gasoline vapor present has a tendency to condense out at temperatures below 40° F. and should any volume of the condensate collect in the pipes it would be a source of danger, in case it passed over to the burners.

Another recent development is the use of mixtures containing less than 2 per cent of gasoline vapor that is below the explosive limit. Such mixtures although low in heating value may be used with a Welsbach mantle without further admixture of air.

Acetylene. The use of acetylene as an illuminant in small towns and for isolated plants has developed to a very considerable extent during the last five years, owing to the standardization that has taken place in the manufacture of calcium carbide, while accurate data cannot be had as to the extent of its use. Brown's Directory of Gas Companies reports 184 acetylene town plants in operation the first of this year. These works report a total output of nearly 19,000,000 feet. It is probable, however, that there are many more plants in existence which did not take the trouble to file their report. To this must be added a very large number of small private plants lighting one or more houses or a factory, and a very considerable quantity of acetylene that is used in the portable tanks for automobile headlights, etc.

Calcium carbide is manufactured in the electric furnace by fusing a mixture of lime and coke. Although acetylene was known chemically as far back as 1836, and in 1862 the formation of calcium carbide was discovered by Woehler, it was not until Wilson's discovery in 1892, that calcium carbide could be commercially manufactured in the electric furnace, that acetylene became of any importance as a possible illuminant.

In the manufacture of calcium carbide, the purity of the raw materials is of great importance and much of the success in the commercial use of acetylene can be attributed to the care taken and the chemical control exercised in the manufacture of the carbide. After fusion in the furnace, the carbide is crushed, sized and packed in hermetically sealed cans. Calcium carbide as formed in the electric furnace is a hard crystalline substance of grayish color and weighs about 138 lbs. per cubic foot.

It is usually packed in cans, holding 200 lbs. The commercial sizes for large generators are 3½ ins. to 2 ins. and for lamps 1 in. to ½ in. and some other smaller sizes running down to dust.

While pure carbide should yield about 5 cu.ft. of acetylene per pound, the yield of gas varies with the size. The larger lumps yield considerably more gas per pound. The British specifications provide

that the standard size 2½ ins. to 1 in. shall yield not less than 4.8 cu.ft. at 60° and 30 ins. bar. with an allowance of 5 per cent for the analysis and that it shall not contain more than 5 per cent of dust that will pass a $\frac{1}{16}$ in. screen. The German specifications provide three grades for sizes down to ⅜ in. The price shall be based on a minimum yield of 4.81 cu.ft. per pound with a 2 per cent allowance for analysis. Carbide yielding not less than 4.33 cu.ft., however, must be accepted with a proportional reduction in price. For the smaller sizes, the base yield is 4.33 cu.ft., and carbide must be accepted that does not yield less than 4.01 cu.ft. The maximum amount of phosphine present in the crude acetylene shall not exceed .04 per cent, with an allowance of .01 per cent for the analysis.

The formation of acetylene from the carbide takes place according to the following reactions:

$$CaC_2+H_2O=C_2H_2+CaO \quad \text{and} \quad CaO+H_2O=Ca(OH)_2.$$

This reaction does not takes place below −5° C., however. This reaction is exothermic, but there is some disagreement as to heat of formation of the acetylene, the net result of the reaction being about 29.1 large calories. This heat of formation is really very important as it must be taken care of in a design of the generator. Acetylene polymerizes very readily at 600° C. into benzol and at higher temperatures forming other complex organic compounds. For this reason, it is essential that ample water should be present to absorb the heat of the reaction or other means must be provided to prevent an excessive rise in temperature. Experiments on the temperatures, occurring in generators, have shown a maximum of from 280 up to as high as 807°, in one case reported by Lewes. Furthermore, at high temperatures, the acetylene may decompose violently, the critical point being about 780°. The heat set free may thus result in an explosion, while if any air is present, it may explode at 480° C. On account of these facts it is exceedingly important that well-designed generators should be used for the generation of the gas. The generators may be divided into two general classes: first, where the carbide is added to the water, second, where the water is added to the carbide. Either of these may be automatic or non-automatic. The American regulations require that the maximum rise shall not exceed 53° C., and that there shall be present at least 8¼ lbs. of water per pound of carbide. While for the hand-fed generators the rise shall not be over 91° C.

Owing to the rise of temperature in the generator, considerable water is vaporized and passes off with the gas, so that a generator requires considerably more water than is indicated by the reaction, the usual allowance being about half a gallon per pound of carbide.

Pure acetylene has a sp. gr. of .9056; its critical temperature is 37° C.

and the critical pressure 68 atmos. The specific heat is .373 and its calorific value is 1440 B.T.Us. per cubic foot. When mixed with air, it ignites at about 430° C. Its explosive limit varies from about 2.5 to 55 per cent.

At 15° C. it is soluble volume for volume in pure water, but the presence of lime or sodium salts in the water such as would exist in the generator, reduces the solubility to about one-third of this figure. Above two atmospheres pressure and at 780° C. acetylene is very unstable and is likely to decompose violently. For this reason liquefied acetylene is very dangerous and its use is generally prohibited. Various solvents such as acetone will take up large volumes of acetylene and this property is made use of in the portable tanks used for automobile headlights. The tanks are filled with a porous material, containing about 80 per cent of voids, about 43 per cent of these are filled with acetone. The acetylene is then compressed into the cylinder at a pressure of 10 atmos., at which pressure the cylinder will hold about one hundred times its volume of acetylene.

Crude acetylene, when first generated from the carbide, contains ammonia, hydrogen sulphide and phosphine, which must be removed before the gas can be used for indoor illumination. The average quantities in the crude gas are probably as follows:

Ammonia	100 to 175 grs. per 100 cu.ft.
Hydrogen sulphide	10 to 50 " "
Phosphine	20 to 40 " "

The ammonia is readily removed by the water in the holder that is usually a part of each generator, but the phosphine, which is the most noxious impurity, must be treated chemically. Various purifying materials have been proposed, most of them based on mixtures of bleaching powder, slaked lime and some other chemical which gives them a claim for being novel. Another material which seems to have given fair success is known as heritol. It is composed of kieselguhr, saturated with an acetic or hydrochloric acid solution of chromic acid. This latter material has an advantage, due to the fact that it changes in color when saturated with the impurity.

Purified acetylene is usually burned to give a luminous flame and owing to the richness of the gas, it is necessary to employ small burners, or else make extra provision for injecting air into the body of the flame by the action of the issuing gas. A usual form of burner has two jets, which impinge and form a flat flame, thus drawing air in on all sides. To assist in the injection of the air and to overcome the high sp. gr. of the acetylene, requires a rather high pressure, considerably higher than that required for coal gas. When burned in such an open flame burner at low rates, the horizontal candle power, if computed at a rate of five feet per hour, would give from 240 to 250 candle power. Cal-

culated on the candle power per foot per hour, it seems to give about 40 candle power. The comparatively high efficiency of the acetylene flame is due not only to its high carbon content, but also to its very high flame temperature, which results in part from the strongly endothermic nature of the gas, disengaging a large quantity of heat when it is dissociated. Mahler gives the flame temperature at 2350°C while Le Chatelier estimates it from 2100 to 2400°C. This is reflected in the high duty obtained when acetylene is burned in a Welsbach mantle where from 120 to 140 candles per foot are obtained.

Owing to the relatively high cost of the heat units in acetylene, it is not an economical fuel, but stoves are now on the market which utilize its high heating value (1440 B.T.Us.) very efficiently and satisfactorily, and in isolated localities, where it is already employed for lighting, it may serve a very useful purpose where economy is not of prime importance.

In connection with the distribution of acetylene care must be taken to insure perfect tightness in the distributing system, owing to the high value of the gas. The use of copper wherever the gas may come in contact with it, must be avoided, as acetylene forms a very explosive compound when brought into contact with copper. This compound is known as copper acetylide, a body to which Blochmann's formula $C_2H_2Cu_2O$ is generally ascribed.[1]

Fig. 251.—Methane-Hydrogen Generator.

Methane-Hydrogen Gas. There are a number of special processes which have been developed to furnish gas either from by-products or for special purposes; among these is the so-called methane-hydrogen gas, which was designed to utilize tar. The cross-section of the generator, Fig. 251, is shown in the cut. The tar is sprayed into the combustion chamber, where it is vaporized, and then passes through the bed of fuel, which is raised to incandescence by an air blast. In contact with the carbon, the ring compounds from the tar are decomposed. The principal product is hydrogen, together with 10 or 15 per cent of methane, carbon monoxide and a small percentage of illuminants. While the

[1] Acetylene: P.A. Oct. 15, 1908, p. 609; G.W., June 20, 1908, p. 780; L.J., June 9, 1908, p. 633; L.J., June 19, 1906, p. 781; Eng., March 2, 1906, p. 261; En.M., May, 1904, p. 259; P.A., Nov. 2, 1903, p. 528.

illuminating value of the gas is low, it can be readily enriched with benzol, if required, and furnishes a commercial solution for the gasification of tar or the manufacture of a low grade of gas. Analyses of this gas show about the following composition:

Illuminants	3	per cent
Carbon monoxide	15	"
Hydrogen	64.2	"
CH_4	12	"
C_2H_6	0	"
CO_2	2.3	"
Oxygen	.2	"
Nitrogen	3	"
Candle power	11	"
B.T.U.'s	400.[1]	"

The same principle is utilized in the Rincker and Wolter system, which was designed to utilize tar and heavy oil residues which could not be handled in the ordinary carburetted water gas apparatus. A mixture of two parts of oil residue and one part of water gas tar is sprayed downward on the bed of heated fuel, decomposing the hydrocarbons. The free carbon, which is liberated, settles on the coke and is burned during blasting. They claim a composition as follows:

Illuminants	8.8	per cent
CO	3.3	"
H_2	59.2	"
CH_4	17.9	"
CO_2	1.0	"
Oxygen	.3	"
Nitrogen	9.5	"

The calorific value may be varied between 350 and 650 B.T.U.'s. A mixture of equal parts of coal tar, water gas tar and Java residue would yield about 20,000 ft. per ton of 500 B.T.U. gas. This process can be varied so that the more complete decomposition is secured and a high yield of hydrogen obtained, thus making a gas suitable for balloon purposes.

Balloon Gas. Owing to increased interest in aeronautics, there is a demand now for gas suitable for inflating balloons. Such a gas should have a low gravity so as to have a minimum lifting power of about 43.6 lbs. per thousand cubic feet. This would correspond to a gravity of .43. Apparently, a gravity of about .33 is considered the most efficient,

[1] Methane hydrogen: L.J., April 25, 1905, p. 225.
Rincker-Walter: Le G.C., Feb. 5, 1910, p. 271; L.J., Nov. 24, 1908, p. 553.
Balloon Coal Gas: L.J.: Aug. 23, 1910, p. 512.
Illum. Gas Processes: E.N., Dec. 9, 1909, p. 640; P.A., April 15, 1909, p. 324.

owing probably to the greater loss by diffusion through the fabric if lighter gravities were used. A nuumber of processes have been devised to prepare suitable gases with the ordinary manufacturing apparatus. Such a process has been patented where the standard form of carburetted water gas apparatus is used. In carrying out this process the fire is carried low, and just enough steam is admitted to prevent burning out the grate bars and to keep down clinker. After the fire has been brought to a working temperature with the blast, from 15 to 20 per cent of the oil is admitted to the top of the fire. This purges the set of the heavy products of combustion. The stack-valve is then closed and the remainder of the oil admitted. The valves are reversed and a small amount of steam is turned on under the fire, which passing up through the fuel bed generates water gas, clears the machine of the oil gas and is used to reduce the gravity to the point desired. The oil, partially decomposed in the fuel bed is completely decomposed in the fixing chambers, due to their very high temperature. In this way the illuminants which have an injurious action on the rubberized fabric are practically eliminated, and by suitably varying the amount of steam any desired gravity may be made. Two analyses of this gas show the possibility of varying the gravity:

Illuminants	1	and	.4	per cent.
CO	15.3	"	5.2	"
Hydrogen	63.7	"	75.4	"
Methane	11.0	"	10.4	"
Ethane	.8	"	.0	"
Carbon dioxide	2.6	"	1.0	"
Oxygen	.5	"	.6	"
Nitrogen	5.1	"	7.0	"
Specific gravity	.37	"	.35	"

Another process for manufacturing a very low gravity gas depends on the decomposition of ordinary coal gas by passing it through hot coke in a retort. The retort is raised to a temperature of about 1200° C. A 10-ft. retort will produce about 300 cu.ft. of gas per hour, the gravity depending somewhat upon the quality of the coal gas, ranging from .22 to .3. Its analysis is about as follows:

Illuminants	nil	
CO	7.3	per cent.
Hydrogen	80.7	"
Methane	6.9	"
CO_2	nil	
O_2	nil	
Nitrogen	5.1	"

General Processes. We have heretofore considered only the manufacture and purification of the several commercial gases, as these processes have differed considerably for each class. We will now take up several steps that while they more properly belong to the distribution of the gas, yet they are undertaken at the plant and may now be briefly considered here as being common to all the various classes.

After the gas passes the purifier it is metered in order that a proper check may be kept upon manufacturing operations. The volume of gas made is usually corrected to 60° F.

The usual form of meter in use, Fig. 252, is the wet drum meter, which

FIG. 252.—Station Meters.

operates by the displacement of a water sealed drum, and this is the only form of meter that actually isolates a definite volume of the gas and records it. Recently, the so-called dry rotary meter has been introduced. In this form the velocity of the gas passing through definite orifices is measured and recorded by a form of anemometer. Another form of meter which has just been introduced is the electric meter, which automatically records the mass, and therefore volume, at a definite temperature of the gas by the rise in temperature of the stream of the gas that has had a definite quantity of heat added electrically. In large installations, particularly in the coke oven industry, where large volumes of gas have to be measured and absolute accuracy is not required, Venturi meters have been used with automatic integrating mechanism. These have been successfully

used where the flow is fairly uniform and their use was desirable owing to low installation cost.

The analytical control of the gas is generally confined to tests for the presence of sulphuretted hydrogen, which are made by allowing a stream of the gas to impinge upon a piece of paper treated with a lead acetate solution.

Gas Analysis. The organic sulphur compounds are determined by burning a definite quantity of the gas in an atmosphere of ammonia. The products are condensed and the sulphur determined as sulphate by precipitating with barium chloride. In the analysis of the gas itself for its constituents, a modified form of Hempel apparatus is usually employed. The burette is provided with a manometer tube and water jacket, which enables the volume to be corrected automatically to a definite temperature and pressure. The constituents usually determined are illuminants by absorption in bromine water, carbon monoxide by absorption in an acid solution of cuprous chloride, CO_2 by absorption in potassium hydroxide and oxygen by treatment with yellow phosphorus. After the absorptions are completed, a portion of the residue is mixed with air and exploded, and the contraction and CO_2 formed determined.

Another portion of the residue is mixed with air and subjected to partial combustion over palladium black, the contraction and CO_2 formed being again determined. From this data it is possible to calculate the percentages of hydrogen, methane, ethane and any residual CO which may have escaped the absorption.

The nitrogen is determined by difference, and is checked by determining the amount left in the residue from the explosion.

While a number of methods have been proposed for the determination of the benzol vapors in the gas, none of them have given very satisfactory results. The more accurate method of Pfeiffer, in which the benzol is nitrated and then determined volumetrically, is very slow and tedious, while the methods of Dennis and O'Neil and St. Clair Deville do not apparently give satisfactory results. Attention is called to a paper by Mr. E. A. Earnshaw, Franklin Institute, for details in the analysis of gases.

The illuminating value is usually determined with a Bunsen photometer, Fig. 253, using the Leeson Star disks in the comparison head. The pentane lamp is now considered the standard of light of the American Gas Industry. Its value as compared with other sources is given in the table below:

VALUE OF INTERNATIONAL CANDLES

(See *Electrical World*, May 27, 1909, p. 1259)

1 pentane candle = 1 Bougie decimale;
= 1 American candle;
= 1.11 Hefner unit;
= .104 Corcel unit.

In connection with the determination of the illuminating value, attention is called to the report of the Committee on Photometry, presented to the American Gas Inst., 1907. The calorific value of the gas is usually determined in a Junker, or modified Junker, calorimeter. For details regarding the standard methods of conducting this test, recourse should be had to the report of the Committee on Calorimetry of the American Gas Inst. for the years 1908 et seq. See also Chapter IV.

Utilization of Residuals. The residuals that are extracted in the course of the purification of the coal gas are worked up differently according to

FIG. 253.—Photometer Room. Also showing apparatus for testing sulphur content.

the local conditions. In many of the smaller plants the ammonia liquor is sold as a crude liquor containing from 1 to 1½ per cent of ammonia. This, of course, entails heavy freight on the large diluting bulk of water, so that now the crude is generally concentrated. A sketch of the form of apparatus frequently used is given in Fig. 254. In this apparatus the crude liquor is first heated by steam to drive off the volatile ammonia. It is then treated with milk of lime and heated further to decompose the fixed ammonium salts. The vapor is condensed and carries the ammonia in solution. This results in a liquor containing upwards of 15 to 20 per cent of ammonia, so that it will stand shipment for a considerable distance to the refining plant.

ANALYSIS OF AMMONIA LIQUOR

	Crude Weak Liquor.	Concentrated Liquor.
	%	%
Ammonia: Neutral carbonate	1.49	29.2
Acid carbonate	6.51	tr.
Sulphide	.49	8.73
Sulphate	.32	
Chloride	2.03	
Hydrate		2.22
Sulphocyanide	.21	
Thiosulphate	.17	
Ferricyanide	tr.	
Total ammonia in liquor	2.5	15.79

In a few plants in this country the liquor is worked up into ammonium sulphate. A sketch of the apparatus, Fig. 255, used for this purpose shows that the ammonia is driven off in the same manner as in the concentrator, but the gas is absorbed in sulphuric acid in what is known as a saturator. The solution of ammonium sulphate thus formed is brought to such a strength that the salt crystallizes out. The wet salt is removed and centrifuged to eliminate the water.[1]

Fig. 254.—Ammonia Concentrator.

The utilization of coal tar has developed into such an important industry that it is only undertaken at a few of the larger plants. It is generally sold as crude tar, to the nearest refiners, where it is worked up, being distilled into four of five crude fractions. The residue remaining after the distillation of the fraction is sold as refined tar for treating roads and other purposes, or pitch. These crude fractions are further treated by distillation, washing with sulphuric acid and soda, and yield refined products after further distillation

[1] Ammonia: P.A., May 1, 1911, p. 37; P.A., July 1, 1909, p. 522; P.A.G.I., 1911; P.A., April 15, 1910, p. 308; L.J., Nov. 15, 1910, p. 474; L.J., May 21, 1907, p. 523.

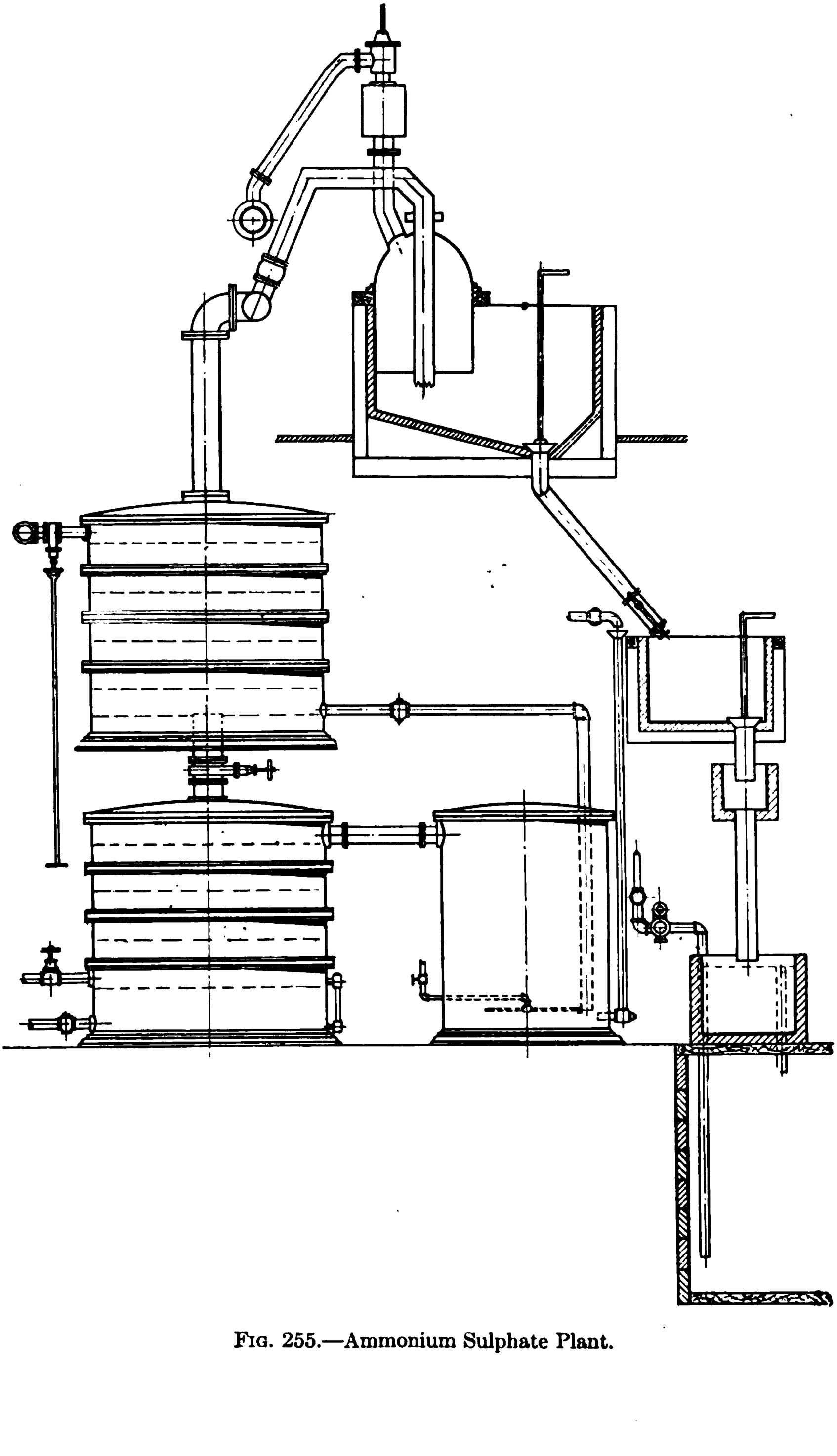

FIG. 255.—Ammonium Sulphate Plant.

such as benzol, toluol and xylol. The first fractions are usually redistilled and carbolic acid compounds, creosoting oil and other products obtained.[1]

Where the cyanogen is extracted it is worked up according to the process in use; that employed by the British Cyanides Co. produces ammonia and ammonia sulpho-cyanide, which is then converted into potassium cyanide or ferro-cyanide; the Bueb system recovers the cyanogen as Prussian blue and ammonium sulphate. The Prussian blue is decomposed, and potassium ferrocyanide is formed.

FIG. 256.—Showing the Gasometers filled and ready for the consumer.

The spent oxide from the purifiers, which contains considerable quantities of free sulphur, Prussian blue and ammonium salts, is usually worked up for the ammonium salts and the cyanogen, as the presence of the tar renders it valueless for the production of sulphuric acid.

[1] Tar: P.A.S.C.E., Jan. 11, p. 140; G.W., April 29, 1911, p. 529; P.A.G.I., 1911; G.W., June 25, 1910, p. 871; P.A.G.I., 1909, p. 333; C.E., Sept. 1909.

Cyanogen: P.A.G.I., 1910, p. 221; L.J., March 24, 1908, p. 767; L.J., Dec. 17, 1907, p. 841; L.J., May 5, 1903, p. 294; L.J., April 21, 1903, p. 156; Die Technologie der Cyanverbindungen Beitelsmann Cyanide Industrie, Robine and Lenglen.

XXII

COAL TAR AND ITS DISTILLATION PRODUCTS

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Coal Tar. This is the black, foul-smelling, oily mixture which separates from the gases formed in the destructive distillation of coal. The raw tar is composed of light oils, pyridine bases, phenols, naphthalene, anthracene, heavy oils, pitch, complex organic compounds insoluble in benzene, and known as free carbon, water, ammonia, and dissolved constituents of the gas. It varies greatly in composition and may be divided into retort gas tar and oven gas tar, according to its method of production.

Retort Gas Tar. This tar is obtained as a condensation product in the hydraulic mains, scrubbers, or condensers, in the manufacture of coal gas for illuminating purposes. It is less fluid and contains less of the lighter hydrocarbons, more naphthalene, anthracene and their accompanying oils, and more free carbon than tars from some other sources. The composition varies with the heats and coals employed. The lower the carbonization temperature of any coal the more fluid the tar and the lower the free carbon content.

The specific gravity of the dry (water-free) tar varies from 1.10 to 1.25 or even somewhat higher.

It contains from 20 to 40 per cent of free carbon and yields on distillation from 1 to 5 per cent of light oil to about 200° C., 30 to 50 per cent heavy oil, including naphthalene, anthracene, phenols, and accompanying oils, from 200° C. to the coking temperature, and from 45 to 65 per cent coke; or if distilled to pitch the yield would be light oil 1 to 5 per cent, heavy oil 25 to 40 per cent, and pitch 50 to 75 per cent.

Oven Gas Tar. This material is obtained as a by-product in the distillation of coal in retort coke ovens. It is similar to retort gas tar, except that it is more fluid. It contains more of the hydrocarbons, and considerably less free carbon, which latter usually runs from 12 to 20 per cent.

The composition of course changes with the coal, with type of oven, and with the coking temperature.

Blast Furnace and Producer Gas Tars. These are of no commercial importance in this country and will not be considered. Owing to the low heats these products are entirely different and in most cases will be useless for the purposes for which coal tar is used.

Water Gas Tar. From the manufacture of carburetted water gas for illuminating purposes, the tar obtained differs mainly from coal tar in the entire absence of tar acids (the phenol group), ammoniacal liquor, and in the small amount of free carbon present, which is usually less than 2 per cent in these tars.

The specific gravity varies from 1.005 to 1.15, but is usually between 1.03 and 1.12 in tars from the larger and more carefully supervised works.

Dry water gas tar, when distilled, yields from 5 to 15 per cent of light oil to 200° C., 30 to 50 per cent of heavy oil from 200° C. to pitch, and 35 to 60 per cent of pitch.

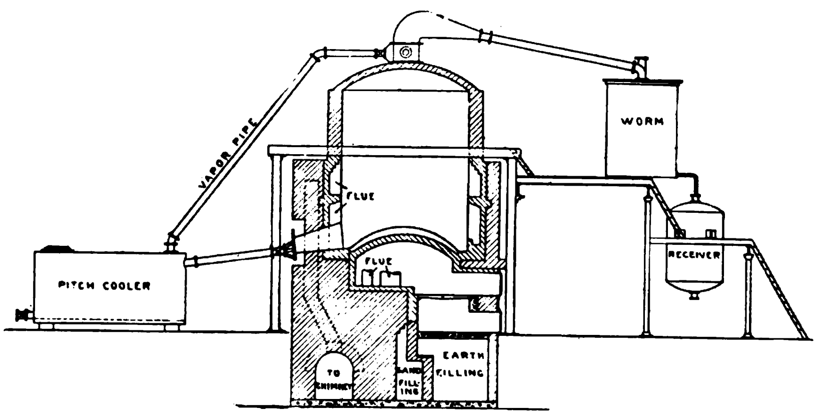

FIG. 257.—European Tar Still.

Pintsch or Oil Gas Tar. This comes from the manufacture of oil gas used for railway lighting. It is similar to water gas tar, but contains much larger amounts of free carbon, frequently 25 to 30 per cent, or even more.

Application of Tar. Tar is little used in the crude state, but is refined by removing the water and more or less oil by distillation. In this condition it is used to saturate roofing felt, to coat roofs laid with plain tar felt, as a cheap paint, and to coat wood which is to be buried in the ground. With more oil removed it is used as a binder in asphalt pavements and tar-macadam roads. With an admixture of water, it is used to sprinkle Telford and Macadam roads to prevent dust.

Tars are separated into their valuable constituents by distillation. The stills, Figs. 257 and 258, may be either horizontal or vertical cylinders set in brick work and heated by direct fire similar to steam boilers. Stills vary in size and in design. Those with a capacity of 10,000 gallons are not uncommon, but most stills have less than half this capacity. The

European practice is to use vertical stills with convex top and concave bottoms.

The top and sides are constructed of half-inch boiler plate, while the bottoms are frequently from 1 to $1\frac{1}{4}$ ins. in thickness and are

FIG. 258.—American Tar Still.

protected from the direct heat of the fire by a brick arch. The hot gases from the fire are led around the lower half of the still in flues.

The American practice is to use horizontal stills heated on slightly less than half of their cylindrical surface protected by an arch directly over the fire and so designed that the portion of the shell heated may be readily replaced when damaged. The still is equipped with the

usual worm, which may be made of either cast- or wrought-iron pipe with receivers, and with a pitch cooler. The objections to cast-iron worms are their numerous joints and greater weight. Since the development of electric welding wrought-iron worms may be made of any desired length with no joints to give trouble. Where high-carbon tars are worked, stills must be provided with suitable means of agitating to prevent the carbon becoming caked upon the heated part of the shell. Drag chains were formerly employed for this purpose, but compressed air or superheated steam are now more often used, as they serve to keep the still clean and assist in removing the high-boiling oils.

Distillation of Tar. The operation of tar stills varies considerably at different works. The receivers are changed at different temperatures and therefore the products are not uniform. In America it is the more common practice to fraction as light oil until the distillate commences to sink in water, and as heavy oil or creosote oil from that point to pitch. Very little, f any, anthracene is made in this country, as most of the tar is run only to soft pitch with a melting-point between 60 and 80° C.

The European practice is different. From four to six fractions are taken before the pitch and a very large percentage of the tar is run to hard pitch. The following will show the most common fractions and the temperatures of the "cuts."

American Practice		European Practice	
Light oil, or Crude naphtha	Till oil sinks in water about 200° C.	First light oil, or First runnings	To 110° C.
		Light oil, or Second light oil	110° to 200° C.
Heavy oil, Dead oil, or Creosote oil	200° C. to pitch	Carbolic oil	200° to 240° C.
		Creosote oil	240° to 270° C.
		Anthracene oil	270° to pitch
Pitch	Residuum	Pitch	Residuum

The tar is usually charged into the hot still (from the previous run).

The fire is lighted when the charging is about half completed. The fire must be carefully regulated till the rumbling or crackling noise in the still ceases, which denotes that the water has all been driven over. The firing can now be pushed so that the distillate runs at the rate of 200 to 400 gallons per hour. When the desired grade of pitch has been obtained, the fire is drawn and the pitch is run or drawn into the pitch cooler, a closed tank with a manhole having a loose-fitting, free-opening lid which, while it acts as a safety valve, prevents free access of air. The pitch, when sufficiently cooled, is filled directly into barrels for shipment or storage.

The fraction to 200° C. contains water, ammoniacal liquor, crude benzols, pyridine bases, and a part of the naphthalene, heavy oil and phenols. The second fraction from 200° C. to soft pitch (about 270° C.) consists of phenols, naphthalene, heavy oil and some anthracene, though

the greater part of the anthracene comes over above 270° C. If the distillation is continued to hard pitch a cut could profitably be made at about 270° C., above which point most of the anthracene and anthracene oil would be obtained. The treatment of the fractions as obtained by the American practice only will be considered with incidental allusions to the foreign methods.

The light oil fraction is allowed to settle and the ammoniacal liquor or water is drawn off. The pyridine bases are not as a rule recovered in this country, but are allowed to remain in the heavy oil with the phenols. If it is desired to separate them the light oil is agitated with dilute sulphuric acid in a lead-lined cone-bottomed tank, fitted with a lead-covered propeller, usually supported entirely outside the tank, which mixes the contents. After the pyridine bases have been removed the oil is transferred to a similar iron tank, in which, in order to remove the phenols, it is treated with caustic soda solution of about 1.116 specific gravity. After the carbolates have been drawn off, the oil is charged in a still, of 2000 to 3000 gallons capacity, similar to a tar still, but having in addition a column and condenser for fractionally condensing, Figs. 259 and 260, and washing the vapors coming from the still. The following fractions are usually taken:

Crude 90 per cent benzol, to 95° C.
Crude toluol, 95 to 125° C.
Crude solvent naphtha, 125 to 170° C.
Heavy naphtha, 170 to 200° C
Residue.

The residue consists of naphthalene, heavy oil, and phenols if not previously extracted. It should be added to the second fraction from the tar still.

In some works only three fractions are made in the light-oil still, the first two being combined and this fraction being subjected before washing to another distillation in a steam-heated column still. The fraction, consisting of benzene, toluene, xylene, and their impurities, would be cut as follows:

Crude 90 per cent benzene....................	up to 95° C.
Intermediate fraction (which is rerun)..........	95 to 105° C.
Crude toluene...............................	105 to 120° C.
Crude solvent naphtha (added to that fraction).	120 to 125° C.

The purification of these fractions consists in the polymerization of the unsaturated compounds and the removal of the dissolved polymerized hydrocarbons by distillation. The oil is treated with successive small portions of sulphuric acid, 1.835 sp.gr., in an agitator tank, Fig. 261, similar to the one used for pyridine extraction. The agitator for washing with strong acid can be lined with lead. A better construction is of cast

iron with leaded joints of the bell-and-spigot type, similar to those used on cast-iron water pipe, and with a conical bottom to permit of complete separation of the acid and the oil. The several small portions of acid are agitated with the oil, allowed to settle for a few minutes and the acid tar composed of spent acid and polymerized hydrocarbons drawn off. Care must be taken to remove the acid tar completely after the final application of acid. The acid necessary for a satisfactory purification of the oil should be determined by a laboratory test after each addition of acid. If too little acid is used the tarry products are apt to separate and clog the draw-off, and if too much is used the spent acid will be very thin and fluid. A good wash is usually obtained when between $\frac{1}{8}$ and $\frac{3}{4}$ of a pound of acid is used per U. S. gallon. This is

Fig. 259.—Benzol Still.

applied in four to six successive portions. In this way a better wash and a larger yield will result together with a saving of acid. Formerly it was usual to wash the oil two or three times with water, but as this serves only to reduce slightly the caustic soda necessary to remove all the acid remaining in the oil, and as it adds materially to the time required to complete the wash, it has been in most cases discontinued. The oil is finally treated with sufficient 10 per cent caustic soda solution to remove all traces of the acid. The washed oil is distilled in a steam-heated still which leaves behind, as a viscid mass, the polymerization products that were dissolved in the oil. This residue is reported to have some application in waterproofing paper.

The final fractioning of the refined oils is conducted in steam-heated stills with columns similar to those used for the rectification of spirits. They consist, Fig. 260, of a series of plates, inclosed in a shell, with nozzles extending from their upper side, over which are inverted saucers or caps

Plan of Bottom of Column

FIG. 260.—Detail of Column.

so designed as thoroughly to mingle the ascending vapors with the descending condensed oils and yet prevent foaming as far as possible.

These columns were formerly made entirely of copper, as is the practice in alcohol rectification, but cast iron, wrought iron and steel are better materials, cost less and are not acted upon by the sulphur compounds contained in the oils. Columns frequently have as many as thirty sections to do the best work, though by far the greater part of the fractioning is done in the first ten or twelve sections.

Benzol. The crude benzols from light oil are colorless when freshly distilled, but they soon become a pale straw color and continue to darken for some time. They are known in the trade as crude or " straw-color " benzols of the various grades.

Fraction.	Specific Gravity.	5–10%	90%	Dry.	Flash-point.
Straw-color benzol....... Crude 90 per cent benzol.	0.860–0.875	80° C.	100° C.	120° C.	below 0° C.
Straw-color toluol....... Crude toluol............	0.860–0.875	100° C.	120° C.	140° C.	below 0° C.
Crude solvent naphtha.....	0.870–0.885	130° C.	160° C.	190° C.	22–26° C.
Heavy naphtha...........	0.925–0.940	160° C.	210° C.	220° C.	43–45° C.

These crude oils are chiefly used as solvents where their odors are not objectionable. Crude solvent naphtha and heavy naphtha are also used as thinners in certain cheap paints.

Of the refined oils three are separated in a pure state, C.P. benzol, C.P. toluol, and xylol. The first two distill entirely within 2° C., while the last is a mixture of the three xylenes and distills from 135 to 145° C.

C.P. benzol or benzene, has sp.gr. .875 to .884. Freezing-point 4° C., boiling-point 80° C. It should distill completely within 2₀ C., be colorless and have the characteristic odor. It should not be colored on shaking with one-half its volume of C.P. sulphuric acid, 1.84 sp.gr., and the acid should be only slightly colored after standing for half an hour. It should be free from thiophens, contain only traces of carbon disulphide and from 1 to 3 per cent of inert paraffines.

Toluol. C.P. toluol or toluene has sp.gr. .865 to .876, boiling-point 110° C. It should be colorless and have the characteristic aromatic odor. It should not be colored by shaking with one-half its volume of C.P. sulphuric acid, sp.gr. 1.84, and the acid layer should not be colored deeper than a pale straw after standing for a half hour. In other respects it should answer the specifications for C.P. benzol.

The following refined commercial fractions are colorless and should not be colored by shaking with one-half their volume of C.P. sulphuric acid, nor should the acid layer become colored deeper than a straw color in one-half an hour except in the case of 160° and 200° naphthas, when the acid may become colored deep red.

Fractions.	Specific Gravity.	Temperatures Noted in Distillation.			Flash-point.
		80° C.–90° C.	100° C.	120° C.	
100% benzol....	0.870–0.880	5–10%–90–95%	dry		below 0° C.
90% benzol....	0.865–0.880	0%	90–92%	dry	below 0° C.
		100° C.	120° C.	135° C.	
50% benzol....	0.862–0.876	50–52%	90–92%	dry	below 0° C.
Commercial toluol	0.865–0.875	10–15%	90–95%	dry	below 0° C.
		130° C.	160° C.	185° C.	
Solvent or 160° naphtha	0.860–0.870	0–10%	90–92%	dry	22 to 26° C.
		160° C.	200° C.	215° C.	
200° naphtha....	0.879–0.882	10–20%	90–92%	dry	42 to 45° C.

The last two are not so well washed, therefore the acid becomes more deeply colored.

In Germany the refined "benzols" are now known as numbers which are compared below to our grades. The distillation of the German grades are also shown.

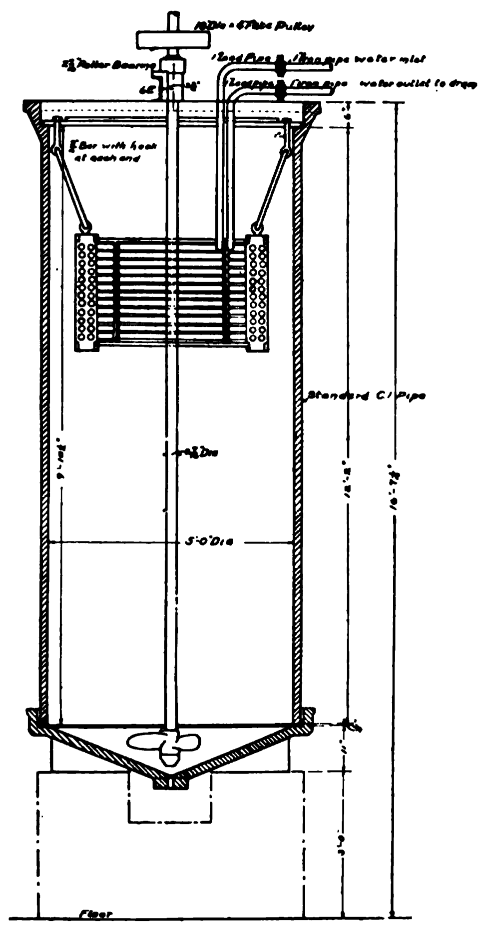

FIG. 261.—Benzol Agitator.

Creosote or Heavy Oil. The fraction from the tar still between 200 and 270° C., and sometimes even higher, contains most of the phenols, naphthalene, anthracene, and the accompanying oils. Anthracene will be found in large quantities only when the distillation of the tar is carried to hard pitch.

If it is desired to remove the tar acids (phenols) the oil is agitated at a temperature of 50 to 70° C. with sufficient caustic soda solution sp.gr. 1.116, to combine with them. The alkaline liquor is allowed to settle and is drawn off, after which the oil is run into shallow tanks or pans, where a large part of the naphthalene separates out as a mass of crystals when the oil cools. It is possible to treat the oil with successive portions of the caustic soda solution so as to obtain, first an alkaline solution in which sodium pheno-

German number	English name	85°	90°	95°	100°	105°	110°	115°	120°	125°	130°	135°	140°	150°	160°	170°	180°	190°
I	90% benzol	48	78	87.5	91.5	....	....	....	dry									
II	50% benzol	....	3		52	67	77	84	90									
III	Commercial toluol	....	....	31	....	11	49	79	91	95								
IV	Carburetting naphtha	....	....	....	....	....	....	....	....	....	30	60	87					
V	Solvent naphtha	....	....	....	....	....	....	....	....	....	....	....	20	75	91			
VI	No. 2 solvent naphtha	....	....	....	....	....	....	....	....	....	....	....	....	5	50	84		
Heavy benzol	200° naphtha	....	....	....	....	....	....	....	....	....	....	....	....	....	....	45	82	91
Technisches benzol	100% benzol	....	90	....	dry													

late preponderates; second an equally pure sodium cresylate; and third an unsaturated solution of caustic soda and sodium cresylate which is used as the first portion on the succeeding charge.

The portion containing principally sodium phenolate is boiled by direct steam, and air is passed through the boiling liquid to remove naphthalene, hydrocarbon oils, and pyridine bases. In some works the distillate from the boiling carbolate is collected and worked for pyridine and naphtha, in which case the boiling is done by fire-heated still instead of by direct steam. The distillate is collected until the purification is nearly complete, when the manhole is opened and direct steam and air blown through the liquor. After this treatment the carbolate of soda should be soluble in water without turbidity. The purified phenolate solution is allowed to become cold and is saturated with carbonic acid gas, usually obtained from the flue gases from the steam boilers. Finally, after the carbonate of soda solution formed has been drawn off, the decomposition is completed, in a lead-lined tank, by a little dilute sulphuric acid, which also aids the separation of the phenol from the aqueous solution. The sodium sulphate solution is carefully and completely drawn off. The crude phenol thus obtained contains from 20 to 25 per cent water and tar. These are removed by distillation in a still similar to a tar still, although much smaller. The dry, crude phenol is fractioned in column stills heated by direct fire or superheated steam, but otherwise the stills are similar to those used for benzols. These yield, first, a crystallizable phenol, second, a fraction not sufficiently rich in phenol to crystallize, and a third fraction containing principally cresols. The fractioning of the crude phenols is conducted at reduced pressure at some works. By this process, owing to the low temperature of the distillation, a larger yield of phenol is obtained.

The crystallizable fraction is further purified by repeated crystallization with the aid of refrigeration and with the addition in the last crystallization of water to dilute the cresols present. Finally, these purified crystals are redistilled, condensed in block-tin worms and collected in tin receivers so arranged that they can be heated to melt the phenol in order that it may run in a liquid state into containers.

A properly purified phenol will remain white for more than a year, showing no trace of the red color commonly seen in crystal carbolic acid.

The second portion of the alkaline liquor from the treatment of the dead oil, containing largely cresylate of soda, is saturated with carbonic and sulphuric acids in the same manner as is the portion rich in phenol. It is not customary to boil the cresylate of soda to remove the oils and pyridine bases unless it is desired to make pure cresol. The crude cresol is freed from tar and water by distillation and is then marketable as 95 to 100 per cent cresylic acid.

Phenol, carbolic acid, hydroxy-benzene, C_6H_5OH, when pure, is a

white, crystalline mass, with sp.gr. 1.084 at 0° C., melting at 42° C., boiling at 182° C., having a characteristic odor and when very dilute a sweetish taste.

It is soluble in all proportions in alcohol, ether, chloroform, glacial acetic acid, and glycerine. It liquefies on the addition of 14 to 15 per cent of water, and thus becomes the No. 4 carbolic acid of commerce. It dissolves in about 20 parts of water at 25° C. It is a corrosive and irritant poison. Undiluted alcohol is one of the best washes for phenol burns. Carbolic acid is largely used in medicine and surgery as an antiseptic and disinfectant and in the arts in the manufacture of dyes. It is employed in the manufacture of picric acid, trinitrophenol, which finds a large use in the manufacture of high explosives, and is also used as a yellow dye.

Cresol, cresylic acid, hydroxytoluene, $C_6H_4CH_3OH$, is a mixture of three isomers, has a sp.gr. of 1.032 to 1.038 at 25° C., and distills between 190° and 205° C. It is used as an antiseptic and disinfectant and is much less corrosive than phenol and is a more efficient antiseptic.[1]

The three isomers composing cresol have the following properties:

Orthocresol, orthocresylic acid, ortho-oxy-toluene, orthomethylphenol, $C_6H_2OH(CH_3)$, with the CH_3 and OH groups in the (1–2) position, is a white crystalline substance melting at 28 to 30° C., into a colorless liquid and boiling at 187 to 189° C. It is soluble in thirty parts of water, in alcohol, ether, chloroform, and the caustic alkalies.

Metacresol, metacresylic acid, meta-oxy-toluene, metamethylphenol, has the CH_3 and OH groups in the (1–3) position, and is a colorless liquid, sp.gr. 1.0498 to 1.05 at 0° C. It boils at 202° C., is soluble in alcohol, ether, chloroform, the caustic alkalies, and slightly in water.

Paracresol, paracresylic acid, para-oxy-toluene, paramethylphenol, with the CH_3 and OH groups placed in the (1–4) position, is a white crystalline mass, melting at 36° C., and boiling at 198° C. It is soluble in alcohol, ether, chloroform, caustic alkalies, and slightly in water.

Xylenol, di-methyl-phenol, hydroxy-xylene. The six possible isomers are probably present in the fraction of crude cresylic acid boiling between 210° and 230° C. and which has a sp.gr. between 1.02 and 1.03 at 15° C. They are on the whole considerably more soluble in water and less corrosive than the cresols. They are principally used in disinfectants of the "creolin" type on account of their high phenol coefficient which is between ten and twelve. They are not generally separated from the cresylic acid except when pure cresols are made.

Naphthalene. The heavy oil fraction, if the removal of the naphthalene is desired, is run into shallow tanks or pans, either from the still or after the tar acids have been extracted, and allowed to become cold,

[1] Dr. A. P. Hitchins has informed me in a private communication that the toxicity of phenol and cresols are directly proportional to their germicidal value and that cresylic acid is about three times as efficient a bactericide as phenol.

when the larger part of the naphthalene crystallizes. The oil is drawn off and the crystals are either shoveled into piles to drain or are passed through a centrifugal which leaves the crystals nearly dry and in condition for market as " drained creosote salts " or crude naphthalene.

Refining naphthalene consists in freeing it from adhering heavy oil and from unsaturated, easily oxidized compounds. The crude material should be in a coarse crystalline condition to allow of the proper extraction of the oil. If it is in a slimy state it should be recrystallized. The crystals are either washed with hot water in centrifugals, which removes the larger part of the adhering oil, or they are hot pressed in hydraulic presses. The latter process is more expensive and less efficient than the former. After this operation the naphthalene should have a melting-point of not less than 76° C., and will still contain from 4 to 6 per cent of oils. The partly purified naphthalene is now distilled, to remove the tarry bodies that have been carried forward from the original tar. This process is conducted in plain, externally fired iron stills, similar to tar stills, but with lead worms. The distillate is kept in a melted state and run into lead-lined agitators similar to those used for benzols, and washed with sulphuric acid, 1.835, sp.gr. several waters, and finally with caustic soda solution, of about 1.116 sp.gr. Great care must be taken to remove as much as possible of the acid before the first water is added, so as to prevent the tarry polymerization products from being redissolved by the naphthalene. The soda solution is drawn off completely, as small amounts of soda will cause the bottom of the still to be rapidly burned out. It is necessary to reject the first portion " heads," and the last portion, " tails," of the distillate from the final distillation of refined naphthalene, as the " heads " are discolored by the washings of the worm and with water containing dissolved bases, metallic salts, etc., while the oils are concentrated in the " tails." The sum of the rejected portions should not exceed ½ to 1 per cent of the distillate.

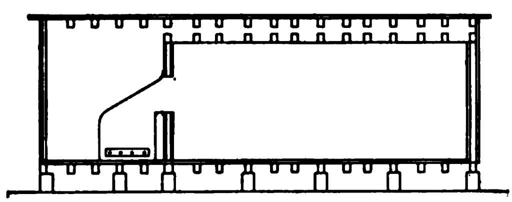

FIG. 262.—Naphthalene Subliming Plant.

The water-white refined naphthalene is run into shallow pans to cool, when it can be broken up and sold as lump, or is run into copper tanks heated by steam, from which it is available for casting into balls, etc., or for use in the subliming pans. Subliming pans, Fig. 262, are large shallow iron tanks heated by steam and connected by an iron hood with a smoothly sheathed room in which the sublimed vapors condense in this transparent plates, " flake naphthalene." About 150° C. seems to be the most satisfactory temperature in the subliming pans. A higher temperature can be economically employed in winter and a somewhat lower one in summer. Naphthalene, $C_{10}H_8$, is a solid hydrocarbon at ordinary temperatures, melting at 79–80° C., and boiling at 218° C. Its specific gravity

in the solid state is 1.151 at 15° C. and in the liquid state it is 0.9778 at 80° C. It volatilizes at ordinary temperatures and very readily on the steam bath. It crystallizes in transparent rhombic plates, which are slightly soluble in hot water but insoluble in cold water. It is very soluble in chloroform, benzene, ether, alcohol, methyl alcohol and paraffine.

The purity of refined naphthalene is indicated by the faint purple or pink tint when a lump is dissolved in hot concentrated sulphuric acid. If the acid is turned a deep red the sample is likely to become discolored on standing. Naphthalene is used as the starting-point of several classes of colors, including nearly all of the azo-colors and for artificial indigo, in candles, celluloid, as a substitute for camphor to prevent moths in woolens, and to some small extent as a gas enricher in lights of the albo-carbon type. It readily nitrates directly to mono-nitro naphthalene, which crystallizes in yellow needles, with sp.gr. 1.331 at 4° C., melting at 56° C., and boiling at 304° C. It is easily soluble in alcohol and petroleum oils. Its principal uses are the manufacture of certain smokeless powders and to remove the fluorescence from petroleum oils, for which latter purpose from 2 to 3 per cent is used.

Anthracene. This oil is the portion of the distillate from coal tar which vaporizes above 270° C. At this temperature a cut should be made if the distillation is carried to hard pitch. This oil boils between 250 and 400° C., and has a specific gravity of nearly 1.1. Its color is yellowish-green when first made, but it darkens to almost black. It contains besides anthracene, naphthalene, methylnaphthalene, pyrene, acridene, phenanthracene, fluorene, etc., all of which are solids, except methylnaphthalene, and a mixture of oils of which we know very little.

The anthracene fraction is run into shallow tanks and the solid compounds separate out on cooling. This process requires from one to two weeks.

Refrigeration has been tried to shorten the time, but it makes the oils more viscid and the separated crude anthracene much more impure. The semi-solid mass is transferred to bag filters or to a filter press and as much as possible of the oil driven out by compressed air. The nearly dry cakes from the bags or filter press, containing about 10 to 15 per cent anthracene, are subjected to a pressure of from 50,000 to 70,000 lbs. in hydraulic presses so arranged that they may be kept hot by steam coils or steam-heated plates. This treatment brings the anthracene content to from 25 to 35 per cent. These press-cakes are ground and purified by washing in a closed agitator with hot solvent naphtha from the light oil.

Lower boiling benzols have been used for this purpose, but they dissolve the anthracene itself. The whole charge, when thoroughly mixed, which may require several hours, is run into a closed filter and the solvent removed by compressed air. Pyridine bases are said to be a better solvent for the anthracene impurities than solvent naphtha and is said to yield 80 per cent anthracene, while 70 to 75 per cent is the limit with solvent naphtha.

A somewhat more pure anthracene is produced by the sublimation of the washed material. The subliming pans are similar to those used for naphthalene except that they are heated by fire and have jets of superheated steam impinging upon the surface of the melted anthracene. The vapors are condensed by water jets The oil from the first crystallization of the crude anthracene is distilled in a clean still till crystals appear upon cooling the distillate, when the residue containing the anthracene is run into pans and treated the same as the original fraction.

When the oil will yield no more anthracene it is used to soften, "cut back," pitch as "Carbolineum Avenarius," for the treatment of timber, and mixed with the creosote oil.

Anthracene, $C_{14}H_{10}$, was discovered by Dumas and Laurent in 1832 and recognized as a characteristic constituent of coal tar by Fritzsche in 1867. It boils at 363° C., melts at 213° C., and has a specific gravity of 1.147 at 15° C. It crystallizes, when pure, in white or yellow rhombic plates with a blue fluorescence. It is soluble in benzene, ether, chloroform, carbon bisulphide, and in hot alcohol, but only sparingly soluble in cold alcohol.

It is slowly converted by sunlight into paranthracene. It is of great importance commercially as the starting-point for the synthetical alizarines.

Valuation of Tar and Tar Products. Sampling is of the utmost importance with the tars and the crude oils. They frequently contain two or more substances that have more or less tendency to separate on standing, such as water and ammoniacal liquor, and which are difficult to reincorporate evenly. Where possible drip samples should be taken as the materials are being pumped.

Small drip openings are so prone to become clogged with particles of dirt or fine crystals that it is always well to make the original drip sample as large as possible. A tank of 100 gallons' capacity can easily be arranged to catch the drip. This can be thoroughly mixed and reduced samples accurately drawn by a large pipette called a "thief." The drip sampling should begin as soon as the pump is working freely and should continue without diminution to the end. With oils that have solidified care should be observed that they are completely remelted and well mixed before drawing a sample. Where it is impossible to take a drip sample a "thief" may be used. A satisfactory "thief" for small tanks or tank cars can be made from a one-inch iron pipe with a round water-way cock, operated by chains, at the lower end. In large tanks and when a proper "thief" is not available, a bottle will serve to obtain a fairly good sample. The bottle is weighted, corked, sunk to the bottom of the tank, when the cork is pulled by a string previously attached and the bottle evenly

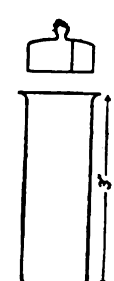

FIG. 263.

and rapidly drawn from the tank. If the bottle is not completely full the sample is considered a representative one. The final samples of tar, light oil, and heavy oil should be not less than one gallon, while a pint usually suffices for naphthas, benzols, etc.

The Examination of Tar. While, as suggested by Allen, Lunge, and others, more definite information can be obtained the larger the scale of operation, yet it has become quite established to work with a gallon sample. The tar sample should be poured into a dish or bucket and mixed by vigorous stirring, to redistribute evenly through the sample any water that may have separated.

The complete examination of tar consists of the following:

Determination of the water by distillation;

Distillation of the tar;

Specific gravity of the dry tar;

Free carbon of dry tar.

Examination of the light oil, heavy oil, and pitch.

The still now largely used in this country for tar distillations and water determinations, Fig. 264, in tar was described by H. W. Jayne (J. A. C. S., XXV., p. 81).

It is made of copper $3\frac{1}{2}$ ins. in diameter, with straight sides 6 ins. high, a heavy turned brass ring at the top, a brass lid, held in place by a single clamp over the top. The lid has two holes, one for a $\frac{1}{4}$-in. pipe plug and the other fitted with a short piece of $\frac{3}{4}$-in. brass pipe tapered on the inside to fit the cork which carries the distilling tube or adapter. This still can be easily cleaned, which is an important provision in a tar still. A paper gasket was used, but the small valve packings similar to vulcabeston are equally satisfactory and may be used repeatedly. The condenser consists of a copper trough through which passes a glass tube about $\frac{1}{2}$ in. internal diameter and 24 ins. long. This form of condenser is ordinarily used without running water. It allows of heating the water when the naphthalene fraction begins to solidify in the tube and drawing it off altogether when the still higher fractions would be liable to crack the glass. It is very efficient for volatile liquids, as the tube can be easily packed with ice or with a freezing mixture. The cut shows the still and condenser mounted for use A larger still $4\frac{1}{2}$ ins. in diameter and 8 ins. high of the same design should be used if 1000 c.c. of tar are distilled or dried.

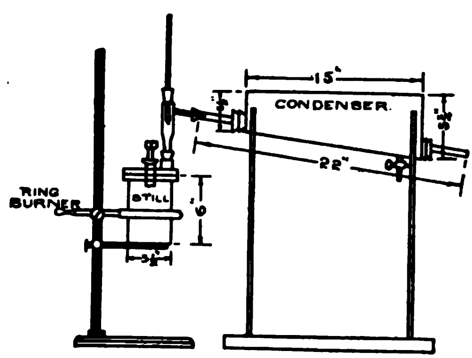

Fig. 264.

The Estimation of Water. Of the well-mixed sample 200 to 600 c.c. is diluted with about 100 c.c. of high-boiling water-free oil. To prevent boiling over, crude solvent or heavy naphtha is usually distilled in the smaller still above described. The heat is at first applied by a ring burner designed to throw the flame toward the still and adjusted so that the flame strikes the still at or above the level of the tar. When the temperature has reached about 150° C., an ordinary Bunsen burner is lighted under the bottom of the still. The distillation is carried to from 200 to 205° C., to be sure that none of the water is held back by the tar or by the apparatus. The distillate is collected in a graduated cylinder and is usually reported as per cent by volume, but if desired may be converted into per cent by weight. The thinning with dry oil may be omitted in many cases and the specific gravity and free carbon can be determined on the dry tar thus obtained after carefully reincorporating the oil carried over by the water.

Specific Gravity. It is obviously quite troublesome, if not impossible, to thoroughly clean the ordinary specific gravity bottle of tar, and there is more tendency for small air bubbles to cling to the sides than in a bottle with vertical sides. For the determination of the specific gravity of tars Lunge has suggested a tall weighing bottle about 1 in. in diameter and 3 ins. high, with a glass stopper having a small vent "v" ground in the joint.

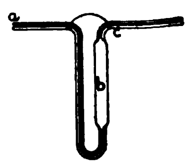

FIG. 265.

The process is the same as for the specific gravity of solids. First fill the tared bottle nearly full of tar, then the balance with water, and finally completely with water. The weighed bottle (a) is two-thirds filled with tar and set in hot water or on a steam bath till the air bubbles have all disappeared. It is then cooled to 15° C. and weighed (b). Water is added to fill the bottle, the stopper forcing out the surplus through the vent; it is carefully dried and the weight taken (c). The bottle is now filled with water at 15° C. and weighed again (d).

$$\text{Sp.gr.} = \frac{b-a}{d+b-(a+c)}.$$

The water and specific gravity of the dry tar are usually a satisfactory index of the quality of the tar. Kohler (Z. angew. Chem., 1888, p. 677) has shown that the specific gravity of dry tar reflects the per cent of free carbon. This complex mixture of organic compounds containing, according to Donath and Asriel, (Chem. Centr., 1903, I., p. 1099), carbon 89.2 per cent, hydrogen 2.3 per cent, nitrogen 0.7 per cent, oxygen 7.13 per cent, ash 0.67 per cent, is quite similar to anthracite coal except for the ash and moisture. It is usual to ascribe a part of this to coal dust carried over from the retorts, but the low ash would seem to preclude more than 8 per cent of coal dust in it.

Free Carbon. Free carbon is, however, one of the most important factors in determining the value of a tar for its more important uses. Many schemes have been proposed for its isolation, based upon different solvents, carbon bisulphide, aniline, glacial acetic acid, and members of the benzene series.

Its determination is always made on the dry tar, and the benzenes are the solvents mostly used in America. The determination is carried out as follows:

One to five grams of tar are weighed in a small beaker, hot toluene added, well mixed and allowed to settle. Two tared S. & S. fat extraction thimbles, the inner one 22×80 mm. and the outer one large enough for a loose fit, are suspended over a beaker or an Erlenmeyer flask, saturated with hot toluene, and the supernatant toluene decanted from the tar through the thimbles. The tar is washed by decantation several times with hot toluene, then three times with hot C.P. benzene, finally the residue is washed into the inner thimble. The thimbles are transferred to a Soxhlet extractor and extracted with benzene. If the benzene becomes too contaminated with tarry extract it is discarded and a fresh portion used to continue the process. When the benzene no longer becomes colored the extraction is complete, the thimbles are dried in a steam bath and finally at 110° C., and weighed.

Volatile Portions. The study of the distillation products of tar is made by distilling 1000 c.c. of the well-mixed sample in a copper still similar in design to those used for the water determination, but with a capacity of 2000 c.c. This distillation is carried by careful heating with a ring burner to 200° C. The distillate is received in a graduated separatory funnel and the percentage of water is noted. The oil is separated and returned to the still as soon as the contents has become cooled to room temperature.

The distillation is started anew and carried to 205° C., when the receiver is changed. The distillation is continued till the residue has a melting-point of 60° C. This is a somewhat troublesome operation, but it is greatly facilitated by collecting the distillate from each 10° C. increase in temperature in separate receivers, usually small graduated cylinders. Thus to cut the residue back to 60° C., if a too high melting-point is obtained, successive fractions may be poured back. When the correct melting-point, 60° C., is reached, the temperature is noted and the pitch is poured into a shallow pan.

The light oil fraction is mixed and its specific gravity taken at 15.5° or 3° C. above the limpid point. A correction of .0008 is added to the specific gravity for each degree above 15.5° C. The tar acids, the phenols, are extracted from the whole fraction if less than 100 c.c. by shaking with one-half its volume of 10 per cent caustic soda solution in a graduated separatory funnel. After carefully separating the soda solution the loss is noted. The treatment with caustic soda is repeated till the loss

becomes constant. This loss equals the tar acids and is usually reported as per cent by volume. The carbolic acid in the soda solution can be set free by dilute sulphuric acid and the volume noted, as a check, 20 per cent being deducted for included water.

The oil free from tar acids is fractioned by a Le Bel-Henninger tube to 170° C., 170 to 200° C., and a residue. The fraction to 170° C. is considered crude benzols, including benzene, toluene, xylene, and solvent naphtha. The second fraction, 170–200° C., is heavy naphtha and the residue is heavy oil. The residue is cooled to 0° C. for 15 minutes and drained on a tared filter paper, by suction, pressed, and weighed. This is the naphthalene often spoken of as pressed naphthalene. The specific gravity and distillation of each fraction, as well as of the residue, should be recorded. As these fractions are often quite small, a 1-c.c. Sprengel specific gravity tube, modified as shown in Fig. 265, with *a* and *c* of capillary tubing, which require no caps, even when the specific gravities of oils as volatile as benzene are taken, has been found accurate and rapid.

The fraction from 200° C. to soft pitch from the original tar is the creosote oil, the specific gravity of which is taken at 15.5° C., or if not limpid at that temperature, 3° above the limpid point, using the same correction factor as for the specific gravity of light oil. A portion of 100 c.c. is distilled in a 200-c.c. distilling flask, noting the distillate at each even 10° C., also at 205 and 315° C. Of this, 90 per cent should be distilled off and the tar acids determined as described for the light oil fraction, the whole 90 c.c. being extracted. The extracted oil is cooled to 0° C. for fifteen minutes and the naphthalene drained, pressed, and weighed as explained above. The per cent of naphthalene is calculated to the weight of the original 100 c.c. of heavy oil.

The Creosoter's test, handed down from English practice, having been specified by Sir Fredk. Abel in the early eighties, with the latest modifications is as follows: Of the melted oil, 100 gms. is weighed into a tared tubulated, 8-oz. retort. A nitrogen-filled thermometer graduated in degrees to 350° C. is fixed in the tubulature with the bottom of the bulb one-half an inch above the surface of the oil. The retort is set on two thicknesses of a 20-mesh wire gauze at least 6 ins. square and the whole bulb and at least 2 ins. of the neck covered with a shield of ⅛-in. thick asbestos board to prevent radiation of the heat. The horizontal distance from the bulb of the thermometer to the end of the condenser tube must not be less than 21 ins., nor more than 24 ins. The fractions are collected in tared bottles or cylinders and weighed. The per cent by weight of the following fractions are reported:

Up to 170° C., water and light oils;
$\left.\begin{array}{l}\text{170 to 200° C.,}\\ \text{200 to 205° C.,}\end{array}\right\}$ light oils and phenols;

205 to 210° C., } naphthalene, naphthalene oil, and phenols;
210 to 235° C., }
235 to 270° C., naphthalene and anthracene oil;
270 to 315° C., anthracene and anthracene oil;
315° C., up, residue in the retort.

For all practical purposes it is sufficient to report the fractions as follows:

Below 200° C., water, light oil, and some phenols;
200 to 210° C., light oil and phenols with some naphthalene;
210 to 235° C., naphthalene, naphthalene oil, and phenols;
235 to 315° C., anthracene, anthracene oil, and some naphthalene;
Above 315° C., residue.

The distillation should be conducted so that it is completed in from thirty-five to forty-five minutes and the fraction 210 to 235° C. is collected in from ten to twelve minutes. The distillation should be made on the dry oil if more than allowed amount of water is present, which varies from 2 to 5 per cent in different specifications. If it is necessary to dry the oil it is done by heating to 205° C. in a retort with a condenser attached. The oil in the distillate is separated from the water and again mixed with that in the retort.

The specific gravity is determined with a hydrometer at a few degrees above the limpid point and the factor .0008 used to correct to 15.5° C.

The U. S. Forestry Service prescribes that the distillation should be made in a special Hempel distilling flask. 250 gms. of the oil are weighed into the tared flask; a loose plug of coarse platinum wire in the constricted portion of the neck supports the 200 large glass beads which partly fill the column. The flask is supported on an asbestos board in which a hole with a notched outline is cut almost as large as the largest diameter of the bulb of the flask. The portion of the bulb above the asbestos board and below the column is covered by an asbestos board box, and an Erlenmeyer-Argand burner is used as the source of heat.

The distillation is run at the rate of one drop per second and the following fractions collected:

Up to 170° C.,	245 to 255° C.,
170 to 205° C.,	255 to 285° C.,
205 to 225° C.,	285 to 295° C.,
225 to 235° C.,	295 to 305° C.,
235 to 245° C.,	305 to 320° C.

The indices of refraction of the different fractions between 235 and 305° C. are determined at 60° C. in a refractometer with light compensator.

The fraction distilling between 305 and 320° C. is treated with four or five times its volume of concentrated sulphuric acid and placed in the steam bath for at least one hour with frequent shaking. It is then transferred to a convenient measuring apparatus graduated in tenths of a cubic centimeter. The flask is rinsed twice with concentrated sulphuric acid and the rinsings added to the main portion. After standing for one hour the unsulphonated oil, if any, is read and the ratio of its volume in cubio centimeters to the weight in grams of the original oil is calculated. The index of refraction of this residue should be low (1.49 to 1.50) and it should not be soluble in 10 per cent caustic soda solution.

The Forest Service have specifications for several grades of creosote oil based on the above analysis. Grade 1 should be derived from the distillation of pure coal tar and free from any adulteration whatever or any undistilled tar.

For water in excess of 3 per cent deduction will be made. It shall have a specific gravity at 60° C. of not less than 1.04. When analyzed by the above method it shall have the following fractions calculated on the moisture-free basis when more than 3 per cent of water is present.

Up to 205° C., not more than 5 per cent.;
Up to 235° C., not more than 40 nor less than 5 per cent;
Up to 250° C., not more than 50 nor less than 15 per cent;
Up to 295° C., not more than 65 nor less than 30 per cent;
At 355° C., the residue must be soft and not sticky.

The sulphonation test of the fraction between 305 and 320° C. shall leave no oily residue insoluble in caustic soda solution.

The indices of refraction at 60° C., shall be as follows for the following fractions:

At 250° C., not less than 1.593, nor more than 1.602;
At 290° C., not less than 1.615, nor more than 1.622;
At 300° C., not less than 1.625, nor more than 1.632.

Grade 2 should be derived from the distillation of coal or water gas tar, or from a mixture of these two. It must not contain any undistilled tar.

If it contains more than 5 per cent of water a reduction in price will be made corresponding to the excess. The specific gravity at 60° C. shall not be less than 1.03. When analyzed by the Forest Service method, it shall have the following fractions calculated on the moisture-free basis:

Up to 205° C., not more than 20 per cent,
Up to 235° C., not more than 55, nor less than 5 per cent;
Up to 250° C., not more than 65, nor less than 15 per cent;
Up to 295° C., not more than 80, nor less than 30 per cent.

The indices of refraction at 60° C. shall be as follows:

At 250° C., not less than 1.59;
At 290° C., not less than 1.602;
At 300° C., not less than 1.61.

The volume in cubic centimeters of the sulphonation residue in the fraction 305 to 320° C. shall not be greater than one-tenth of the weight in grams of the fraction.

Heavy, high-boiling oils only are suitable for open-tank method of treatment, and are also better preservatives. It was customary to specify from 8 to 10 per cent tar acids, but this is not a part of the above Forest Service specifications. There seems to be no doubt that the phenols aid in the preservation of wood by coagulating the albumen, but they do not remain as long in the wood as the higher boiling and solid compounds, such as naphthalene.

Examination of Pitch. Owing to its complex composition and the little that is known about its constituents, the tests that are applied to it are designed to show the relation of certain physical properties in different samples, and are therefore mostly physical. They include specific gravity, evaporation, melting-point, softening-point, breaking-point, slide test and free carbon determination.

The free carbon is determined in the same manner as for tar, the pitch being made into strings before weighing to present a large surface to action of the solvents.

The evaporation is determined by heating in an air bath at 160° C. for seven hours. Ten grams are weighed into a metal dish similar to those used in milk analysis and the loss in weight noted.

The breaking-point is found by fastening several small pieces of pitch to a copper plate by carefully heating it so that the pitch melts slightly and adheres firmly. It is then placed in tepid water and allowed to remain five minutes to acquire the temperature of the water. The point of a small knife blade is slid along the plate till it touches the pitch, then slowly and forcibly raised, edge first, through it. If the pitch is still soft the blade will be shoved through without scaling off any of the pitch.

The temperature is lowered after each trial by the addition of cold water; after standing five minutes the blade is forced through it again.

If the breaking-point is reached the pitch will scale off with a conchoidal fracture.

The melting- or fusing-point has been determined in many different ways, most of which do not agree one with another. The melting-point is not so exact a test by any method that 2 or 3° C. will make any appreciable difference in the general properties of a pitch even from the same source. One method consists in heating water in a copper beaker at the rate of 5° C. per minute and drawing a piece of pitch along

the upper part of the beaker. When the pitch makes a continuous smooth streak the temperature is noted. The temperature is allowed to rise a few degrees and as it again falls the pitch is once more drawn across the beaker and the point noted when it last gives a continuous streak. The two points should occur at the same temperature, which is the melting-point. As much depends upon the pressure with which the pitch is held against the beaker, which cannot be exactly controlled, the method only gives approximate results and cannot be made to check in the hands of different operators.

Buchanan (J. Soc. Chem. Ind., 1894, p. 1098), heats in a dry test-tube a thermometer to which has been stuck a piece of the pitch. The pitch softens and falls off. The size of the piece will influence the result, as will the rapidity of rise of temperature, and as these are not specified it is quite possible for two operators to get widely different results.

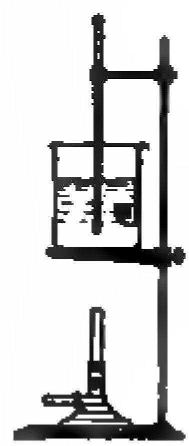

FIG. 266. FIG. 267.

Mabery and Sieplein (J. A. C. S., XXIII, p. 16), devised a method primarily for asphalt, but equally applicable to pitch. A flat metal strip one-half inch wide is suspended in a tall beaker by a cork, as shown in the cut, Fig. 267, with the bottom end turned out at right angles to form a support for the pitch to be tested. The pitch is cut or molded into pieces $1 \times \frac{1}{2} \times \frac{1}{8}$ in., and lays flat on the support so that $\frac{1}{4}$ in. projects on either side. The support is adjusted $\frac{1}{2}$ in. above the bottom of the beaker. The beaker is heated in a glycerine bath and the temperature is noted when the pitch softens, becomes fluid enough to fall down and just touch the bottom of the beaker.

The authors state that there is at the most only 2 or 3° C. variation, and in most cases there are no variations in duplicates. They also expedite matters by making a second test without cooling the glycerine bath, which would seem to tend to raise the melting-point, as only half the time elapses before the melting-point is reached. The authors found it advisable to lay a disk of metal on the bottom of the inner beaker to facilitate cleaning. The support for the pitch being adjusted $\frac{1}{2}$ in. above this plate.

It is quite evident that any method must exactly fix all the conditions as melting- and softening-points are entirely arbitrary in pitch analysis.

Several methods have been devised which depend upon weighting the pitch by mercury, but the variations between duplicates is wider than with the more simple method in most common use, which is described below.

The apparatus, Fig. 266, consists of a mold for making $\frac{1}{2}$-in. cubes of pitch, a beaker of about 600 c.c. capacity, supported on a piece of asbestos board, a thermometer graduated in degrees. Several wires are bent as shown in the cut so as to support the cube of pitch being tested, which is exactly

1 in. from the bottom of the beaker, and a Bunsen burner is so adjusted that the temperature of the liquid in the beaker will be raised 5° C. each minute.

For soft and medium pitches melting below 90° C., distilled water is the bath in which the cube is suspended, but for higher melting-points glycerine, cotton-seed oil, or calcium chloride solution are suitable liquids. Several cubes are supported in the bath so that the under side of each is exactly 1 in. from the bottom of the beaker. A cube is taken out from time to time and twisted with tongs; when one can be readily twisted completely around twice without breaking the softening-point is reached. The melting-point is noted when the cube of pitch drops and just touches the bottom of the beaker. The bulb of the thermometer should be so placed that the bottom of it is at the same height as the bottom of the cube. In the case of low melting-point pitch it is advisable to allow the cube to rest in the bath for five minutes before applying the heat. This method will give duplicates with not more than 2 or 3° maximum variation, even when made by different operators.

As a check on hard pitch, the method described by Dr. Clifford Richardson for asphalts is frequently used. It gives results about 20° C. lower than the cube method. The pitch is cooled, if necessary, and ground in an agate mortar to a fine powder. A small portion of the powdered pitch is transferred to a thin No. 00 microscope cover glass and floated in the surface of a beaker of mercury. The temperature of the mercury is raised 2° C. per minute. The pitch is examined with the aid of a small lens, and the temperature noted when the particles begin to melt.

The slide or flow test, together with the melting- and breaking-points, is designed to give information of the relative fitness of pitches for roofing purposes. A ½-in. cube of pitch is fastened to a grooved copper plate by slightly heating the plate. The plate is then inclined at an angle of 30°, and placed in an air bath kept at exactly 40° C. for twelve hours. The length of the stream of pitch is measured and compared with other samples known to be satisfactory under given conditions. It is quite important that the slide be insulated by asbestos board from the metal of the oven and that the temperature be maintained at exactly 40° C., as slight variations in the temperature will render the results valueless. The grooved plate has several grooves and it is customary to test several samples at once.

The specific gravity of pitch is determined in any manner satisfactory for solids. The weighing bottle previously described for tar will be found a very good substitute for the ordinary specific gravity bottle for this work.

The Examination of Light Oil, Crude Naphthas, and Refined Benzols. The usual requirements of the examination of light oil are met by the tests prescribed for the fraction of the distillate from tar up to 200° C. (see p. 472) but occasionally it is desirable to determine approximately the constituents of the oil and a larger sample, frequently two to four liters, is worked as follows.

The tar acids and pyridines are removed, the former by caustic soda as previously described under the examination of tar, and the pyridines by dilute sulphuric acid, sp.gr. 1.15. The acid solution from the pyridine extraction is heated on a steam bath, water being added from time to time, to replace that lost by evaporation, till the addition of water no longer produces a cloudiness. The bases are then set free by strong caustic soda solution and their volume measured.

If it is desired, the bases suitable for denaturing alcohol can be determined by distilling the above alkaline solution and separated bases until no further trace of pyridine comes over with the distillate.

The distillate is mixed with four times its volume of absolute alcohol. 10 c.c. of this solution is further diluted with 50 c.c. absolute alcohol and agitated with 2 c.c. of a concentrated aqueous solution of cadmium chloride. After twenty-four hours the crystals that have formed are transferred to a tared filter, dried at 100° C., and weighed. The dry crystals contain 46 per cent of pyridine bases that comply with the specifications for denaturing alcohol.

After the phenols and pyridines have been removed, 1000 c.c. of the extracted oil is distilled in a 2000 c.c. copper still, similar in design to those used for tar testing. The still is fitted with a 6-bulb Lebel-Henninger fractioning tube with copper or platinum gauze in the bottom of each bulb to aid in mingling thoroughly the vapor and condensate. The thermometer is adjusted so that the top of the bulb is level with the side tube. Connection is made to a Liebig condenser or one like those described under tar testing and the distillation carried on at the rate of 2 to 3 drops per second.

Fractions are taken

Up to 75° C., low-boiling, unsaturated bodies and some benzene.
75 to 95° C., crude, 90 per cent benzol.
95 to 105° C., intemediate fraction distilling 60–65 to 100° C.
105 to 125° C., crude toluol.
125 to 170° C., crude solvent naphtha boiling 90 per cent to 160° C.
170 to 200° C., crude heavy naphtha boiling about 80–90 per cent to 200° C.

These fractions, except the last, are shaken in a separatory funnel with 1 per cent of concentrated sulphuric acid in two portions. Each portion is vigorously agitated for five minutes and the settled acid tar carefully drawn off. After the second treatment with acid the oil is washed twice with water, then with caustic soda solution 1.116 sp.gr. and finally with water again. The final traces of water may be removed by passing through a dry filter and a distillation made as described below. The distillations are compared with Tables I, II, III, and IV, from which the approximate yield of the various constituents can be computed.

I.—MIXTURES OF BENZENE AND TOLUENE
(Showing the distillation of definite mixtures)

Benzene...	95	90	85	80					55	50	45	40	35	30	25	20	15	10	5	Benzene
Toluene..	5	10	15	20					45	50	55	60	65	70	75	80	85	90	[illegible]	Toluene
81° C.	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	81° C.
82° "	6	2	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	82° "
83° "	65	15	2	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	83° "
84° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	84° "
85° "	87	70	40	8	1	...	...	...	...	...	...	...	...	...	...	...	...	...	...	85° "
86° "	...	...	...	...	...	1	1	...	...	...	...	...	...	...	...	...	...	...	...	86° "
87° "	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...	...	...	...	87° "
88° "	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...	...	...	88° "
89° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	89° "
90° "	95	90	82	74	62	49	37	21	7	1	...	...	...	...	...	...	...	...	...	90° "
91° "	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	...	91° "
92° "	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	...	92° "
93° "	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...	...	93° "
94° "	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	...	94° "
95° "	97	94	91	87	79	75	69	61	51	38	24	7	2	...	...	...	...	...	...	95° "
96° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	...	...	96° "
97° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	97° "
98° "	dry	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	98° "
99° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	99° "
100° "	...	96	94	92	88	85	82	77	72	65	57	48	37	25	8	1	...	...	...	100° "
101° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	...	101° "
102° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	102° "
103° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	103° "
104° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	...	104° "
105° "	...	dry	96	95	93	91	89	87	84	80	77	71	67	60	50	39	21	2	...	105° "
106° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1	106° "
107° "	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	107° "
108° "	...	...	dry	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	108° "
109° "	...	...	...	dry	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	109° "
110° "	...	...	...	...	96	96	95	94	93	92	91	90	88	87	86	84	80	72	53	110° "
111° "	...	...	...	...	dry	dry	dry	dry	dry	97	96	95	95	95	95	95	95	95	95	111° "
112° "	...	...	...	...	...	...	...	...	...	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	112° "

II.—MIXTURES OF TOLUENE AND XYLENE

(Showing the distillation of definite mixtures)

Xylene....	5	10	15	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90	95	Xylene
Toluene...	95	90	85	80	75	70	65	60	55	50	45	40	35	30	25	20	15	10	5	Toluene
111° C.	1																			111° C.
112° "		1																		112° "
113° "			1																	113° "
114° "				1																114° "
115° "	89	69			1															115° "
116° "						1														116° "
117° "							1													117° "
118° "								1												118° "
119° "									1											119° "
120° "	96	92	83	73	61	46	27			1										120° "
121° "																				121° "
122° "											1									122° "
123° "												1								123° "
125° "	dry	96	92	88	83	77	70	60	50	37			1							125° "
126° "														1						126° "
127° "															1					127° "
128° "																				128° "
129° "																				129° "
130° "			95	93	91	88	85	80	76	69	64	54	43	30	15	2				130° "
132° "		dry															1			132° "
134° "																		1		134° "
135° "			96	95	95	93	92	90	87	85	85	81	76	71	61	48	30	8		135° "
136° "																			1	136° "
137° "			dry																	137° "
138° "				dry	96	95	95	94	93	90	90	89	87	86	82	76	68	56	30	138° "
139° "					dry														56	139° "
140° "						97	96	96	95	95	95	95	94	93	92	91	88	84	84	140° "
141° "						dry	dry										95	95	95	141° "
142° "								dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	dry	142° "

III.—MIXTURES OF BENZENE, TOLUENE, AND XYLENE
(Showing the distillation of definite mixtures)

Benzene	80	75	70	65	60	55	50	45	40	35	30	25	20	40	35	30	25	20	Benzene
Toluene	10	15	20	25	30	35	40	45	50	55	60	65	70	40	45	50	55	60	Toluene
Xylene	10	10	10	10	10	10	10	10	10	10	10	10	10	20	20	20	20	20	Xylene
81° C.	1																		81° C.
82° "		1																	82° "
83° "			1																83° "
84° "				1															84° "
85° "	31	7	6	2	1	1													85° "
86° "																			86° "
87° "							1												87° "
88° "																			88° "
89° "																			89° "
90° "	68	56	45	37	19	18	6	1											90° "
91° "									1					1					91° "
92° "										1					1				92° "
93° "																			93° "
94° "											1								94° "
95° "	79	74	68	64	53	48	37	23	12	4	2	1		11	5	1			95° "
96° "													1				1		96° "
98° "																			98° "
100° "	84	80	78	75	69	65	59	51	43	34	22	13	3	35	25	17	6	1	100° "
105° "	87	84	83	81	78	75	72	69	64	59	52	44	33	54	47	40	33	19	105° "
110° "	89	87	86	86	83	82	80	80	77	75	72	68	68	66	63	59	54	47	110° "
115° "	80	88	89	90	88	87	87	87	86	87	86	86	87	76	74	73	72	69	115° "
120° "	91	90	91	91	91	91	92	93	93	94	95	94	95	83	82	83	83	84	120° "
125° "	93	92	93	94	93	94	94	95	95	97	97	97	98	89	89	90	90	91	125° "
130° "	94	94	95	96	96	96	97	98	97	98	98	98	99	94	93	95	95	95	130° "
131° "													dry						131° "
132° "																			132° "
133° "					dry	dry		dry	dry	dry	dry	dry							133° "
134° "		dry	dry				dry												134° "
135° "				dry										97	96	98	98	97	135° "
136° "	dry																		136° "
137° "																dry		dry	137° "
138° "														dry	dry		dry		138° "

IV

MIXTURES OF TOLUENE AND SOLVENT NAPHTHA

(Showing the distillation of definite mixtures)

Toluene	90	80	70	60	50	40	30	20	10	Toluene
Solvent	10	20	30	40	50	60	70	80	90	Solvent
110° C.	1	......	......	......	......	......	......	......	......	110° C.
111° "	......	1	......	......	......	......	......	......	......	111° "
112° "	......	......	1	......	......	......	......	......	......	112° "
114° "	......	......	......	1	......	......	......	......	......	114° "
115° "	82	46	26	3	......	......	......	......	......	115° "
117° "	......	......	......	......	1	......	......	......	......	117° "
119° "	......	......	......	......	......	1	......	......	......	119° "
120° "	93	79	66	42	23	2	1	......	......	120° "
122° "	......	......	......	......	......	......	......	1	......	122° "
125° "	95	89	80	64	52	34	27	4	1	125° "
130° "	96	91	85	77	69	55	42	27	13	130° "
135° "	97	93	89	83	78	70	60	53	34	135° "
140° "	......	94	91	87	84	77	70	64	55	140° "
145° "	98	95	93	90	88	88	79	75	70	145° "
148° "	dry	......	......	......	......	......	......	......	......	148° "
150° "	......	96	94	92	91	89	85	85	80	150° "
155° "	......	97	95	94	94	92	90	89	87	155° "
159° "	......	dry	......	......	......	......	......	......	......	159° "
160° "	......	......	96	95	96	95	93	94	92	160° "
165° "	......	......	......	96	97	97	95	96	94	165° "
166° "	......	......	dry	......	......	......	......	......	......	166° "
169° "	......	......	......	dry	......	......	......	......	......	169° "
170° "	......	......	......	......	......	98	97	97	96	170° "
172° "	......	......	......	......	dry	......	......	......	......	172° "
174° "	......	......	......	......	......	dry	......	......	......	174° "
175° "	......	......	......	......	......	......	99	98	98	175° "
177° "	......	......	......	......	......	......	dry	......	......	177° "
178° "	......	......	......	......	......	......	......	dry	dry	178° "

Mr. G. E. Davis uses the following tables for estimating the probable yield of 50 and 90 per cent benzol and toluol in naphthas.

The distillation of crude and refined benzols is conducted in a 200 c.c. distilling flask with the side tube at the middle of the neck, using 100 c.c. of the sample. The flask should be supported on a 6-in. square sheet of $\frac{1}{8}$-in. asbestos board in which is cut a circular hole 1 in. in diameter.

The asbestos sheet prevents superheating the vapors by radiation when the distillation is ending. In distilling high-boiling oils the bulb of the flask above the supporting sheet of asbestos board should be covered by a box of sheet asbestos to protect the bulb from drafts of cold air. A Bunsen burner is the best source of heat. The thermometer is adjusted with the bulb just below the side tube.

MIXTURES OF 90% WITH 50% BENZOL

By G. E. Davis

Percentage of 90% Benzol.	Percentage of 50% Benzol.	First Drop.	Per Cent at 100° C.	Per Cent at 120° C.
0	100	92° C.	50	90
5	95	92° "	51	92
10	90	91° "	51.5	92
15	85	91° "	53	92
20	80	90° "	55	92
25	75	90° "	60	93
30	70	90° "	65	93
35	65	90° "	67	94
40	60	88° "	69	94
45	55	88° "	70	94
50	50	87° "	71	94
55	45	87° "	73	94
60	40	86° "	76	95
65	35	86° "	78	95
70	30	86° "	79	96
75	25	85° "	84	96
80	20	85° "	84	97
85	15	84° "	86	97
90	10	84° "	88	dry
95	5	84° "	89	dry
100	0	84° "	90	dry

MIXTURES OF 90% BENZOL WITH COMMERCIAL TOLUOL

By G. E. Davis

Per Cent of 90% Benzol.	Per Cent Toluol.	First Drop.	Per Cent at 100° C.	Per Cent at 105° C.	Per Cent at 110° C.	Per Cent at 120° C.
0	100	103°	0	7	50	94
5	95	102°	0	21	59	94
10	90	101°	0	30	66	94
15	85	100°	0	38	68	95
20	80	97°	9	43	73	95
25	75	95°	16	53	76	95
30	70	95°	23	59	78	96
35	65	94°	43	60	80	96
40	60	93°	43	66	82	96
45	55	92°	46	71	85	97
50	50	91°	52	72	86	97
55	45	91°	58	76	86	97
60	40	91°	60	78	88	97
65	35	90°	65	81	89	97
70	30	89°	71	83	91	97
75	25	88°	75	85	91	98
80	20	87°	77	87	92	98
85	15	86°	83	89	93	98
90	10	85°	85	91	94	dry
95	5	84°	88	93	95	dry
100	0	84°	90	94	96	dry

MIXTURES OF 50% BENZOL WITH COMMERCIAL TOLUOL

By G. E. Davis

Per Cent 50% Benzol.	Per Cent Toluol.	First Drop.	Per Cent at 100° C.	Per Cent at 105° C.	Per Cent at 110° C.	Per Cent at 120° C.
100	0	92°	50	68	80	91
95	5	93°	45	64	76	91
90	10	94°	33	60	73	90
85	15	94°	30	58	73	90
80	20	95°	28	57	72	90
75	25	95°	26	55	71	90
70	30	96°	22	48	67	90
65	35	96°	19	47	65	90
60	40	96°	15	46	65	90
55	45	97°	12	44	65	90
50	50	98°	8	42	64	90
45	55	98°	4	34	57	90
40	60	99°	0	26	56	90
35	65	100°	0	25	55	90
30	70	100°	0	23	53	90
25	75	100°	0	21	53	90
20	80	100°	0	16	48	90
15	85	101°	0	14	46	90
10	90	102°	0	13	45	90
5	95	103°	0	10	44	90
0	100	103°	0	0	39	90

The distillation is conducted at the rate of about two drops per second, so that the whole 100 c.c. distills in 20 to 25 minutes. The first drop falling from the condenser is noted as 1 c.c. and the amount collected at each 5° is noted. For the ordinary commercial benzols a thermometer graduated in degrees is satisfactory, but for pure benzol and toluol the graduations should be $\frac{1}{10}$ degree centigrade. Commercial benzols may contain sulphurous acid set free from unstable compounds formed in washing. A strip of moistened iodide of starch paper may be hung at the mouth of the condenser to detect it.

The barometer materially influences the boiling-point of pure benzol, toluol, and xylol, and a correction of the observed thermometric reading must be made by adding if below 760 mm. and subtracting if above that pressure the product of the difference in millimeters from the standard barometric pressure by one of the following factors: for pure benzene, 0.043, for toluene, 0.047, and for xylene, 0.052.

The tar production of the world was summarized, in an article by Russig in the *Chemische Zeitschrift*, as 1,899,400 tons in 1900, exclusive of blast-furnace and water-gas tars. The U. S. Census reports the following as the production of the United States:

	1900	1905
Coal gas tar	60,900 tons	77,643 tons
Coke oven tar	47,500 "	131,117 "
Water gas tar	342,306 "	259,934 "
The census also reports as used:		
Coal tar	110,323 "	127,732 "
Water gas tar	....	117,459 "
There were imported:		
Crude tar and pitch	80,047 barrels	46,057 barrels
Estimated to equal in tons	18,341	12,722

Statements have been made that only 20 to 30 per cent of the tar produced in the United States was taken by the tar distillers. From the figures above it would seem that all of the coal tar and a large portion of the water-gas tar was used by the distillers.

XXIII

THE PETROLEUM INDUSTRY

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Petroleum. Petroleum, from two Latin words: *Petra*, a rock, and *Oleum*, oil, is an inflammable oily liquid of characteristic odor, generally found in large quantities in porous rocks called sandstones—of practically all geological ages of the earth's crust from the Lower Silurian to the latter part of the Tertiary, and is usually overlaid by an impervious formation. In appearance it varies widely, some being found of light yellow color and very limpid, while others are almost black and of high viscosity. The specific gravity, according to Redwood,[1] varies from 0.771 to 1.06 (51.5 to 2.3° Beaumé).

The occurrence of petroleum has been known since 450 B.C.[2] at Kirab, in Persia. The early settlers in America found the Seneca Indians gathering it from what is now Oil Creek, near Oil City, Pennsylvania. It was also associated with the brine from the salt wells of the Kanawha Valley in West Virginia.

Mr. George H. Bissell, a New York lawyer, was the first man to propose drilling for oil, and in 1858 the Seneca Oil Co., organized by him, engaged the services of Mr. E. L. Drake as superintendent, and started operations on a plot of ground leased from the Pennsylvania Rock Oil Company. After many delays they were finally rewarded by striking a 25-barrel[3] well at a depth of 69 ft., in August, 1859. This marked the beginning of the petroleum industry.

Origin of Petroleum. The origin[4] of petroleum has been the subject of much discussion among scientists throughout the world, the theories set forth being divided into two groups the inorganic and the organic. The inorganic theories consider petroleum to have been produced by the reaction of inorganic substances. Berthelot believed it to have been formed by the action of steam and carbon dioxide on highly heated alkali metals, which, according to Daubree's hypothesis, were supposed to exist in the

[1] "Petroleum and its Products," by Sir Boverton Redwood.

[2] The early writings of Herodotus; Bibliography of the Annual Report of the Geo. Survey of Penna., 1886.

[3] A well yielding twenty-five 42-gallon barrels per day.

[4] For a more detailed description of the origin of petroleum, the reader is referred to "Petroleum and its Products," Vol. I, Sir Boverton Redwood.

depths of the earth. Mendelejeff believed it to have been formed by the action of water on highly heated metallic carbides. These theories have been supported by laboratory experiments, yet they are not in accord with the geological conditions under which petroleum is found.

The organic theories that petroleum has resulted from the decomposition of either animal or vegetable matter, or both, are now generally accepted. They have also been supported by laboratory experiments, and comply more fully with the views held by the geologists. Peckham[1] believed that petroleum was produced by the slow distillation of animal and vegetable matter at a low temperature; Phillips[2] and Sterry Hunt,[3] that it was due to the decomposition of vegetable matter under water and in the absence of air. Orton[4] considered Pennsylvania petroleum to have been derived from organic matter of bituminous shale, probably vegetable; and Canadian oil produced from limestone, probably animal.

Constitution. Crude petroleum consists essentially of a complex mixture of hydrocarbons of different boiling points, often accompanied by small percentages of oxygen, sulphur, and nitrogen compounds. The oils produced from different localities often vary widely in chemical composition, but they are all refined by the same general methods.

The following table[5] given by F. W. Bushong shows the ultimate chemical composition of samples obtained from different localities:

Sp.Gr.	Field.	Carbon.	Hydrogen.	Sulphur.	Nitrogen.
......	Pennsylvania (235)	86.06	13.89	0.06	....
0.8095	Oil City, Pa. (236)	85.80	14.04	....	....
0.8367	Welker, Ohio (236)	85.46	13.91	0.48	....
0.836	Findlay, Ohio (236)	84.57	13.62	0.72	0.11
0.862	Petrolia, Canada (236)	83.94	13.37	0.99	....
0.865	Cherryvale, Kan. (237)	85.43	13.07	0.37	....
......	Baku, Russia (235)	86.25	13.48	....	....
0.912	Humboldt, Kan. (237)	85.63	12.44	0.37	....
0.912	Beaumont, Tex. (238)	85.05	12.30	1.75	....
0.912	Ventura, Cal. (239)	84.00	12.70	0.40	1.70
0.940	Humboldt, Kan. (237)	85.33	11.80	0.15	....
0.9458	McKittrick, Cal. (240)	86.06	11.45	0.87	....
0.9845	Santa Barbara, Cal. (236)	86.32	11.70	0.84	....

235 Engler, Ber. d. Deutsch. Chem. Ges., 28, 2501, 1895.
236 Mabery, Amer. Chem. Jr. 17, 713, 1895; 18, 55, 149, 1896; Proc. Amer. Acad. A. and S., 40, 323, 1904.
237 Bartow and McCollum, Trans. Kan. Acad. Sci., 19, 58, 1903.
238 Richardson, Jr. Franklin Inst., 113, 162, 1900.
239 18th Ann. Rep. U. S. G. S., 842, 1896–97.
240 O'Neill, Jr. Amer. Chem. Soc., 25, 699, 1903.

The oil refiner divides petroleum into two general classes, viz.: the "paraffin-base," those yielding solid hydrocarbons of the paraffin series

[1] United States Census Report, 1880.
[2] Phillips Amer. Chem., XVI, p. 429.
[3] Bull. Soc. Geol., XXIV, p. 570.
[4] Report on the occurrence of petroleum, natural gas, and asphalt rock in Western Kentucky, 1892.
[5] University Geol. Survey of Kansas, Vol. IX, 1908.

C_nH_{2n+2}; and the "asphaltic-base," or those rich in asphalt and containing practically no solid paraffins. There is, however, no sharp line of distinction, as some of the oils from Kansas, Oklahoma, Northern Texas, and Illinois contain both asphalt and paraffin.

Locality. The oil from Pennsylvania, of the Appalachian field, which includes Pennsylvania, New York, Southeastern Ohio, West Virginia, and Kentucky, is generally considered the best grade of petroleum produced in large quantities. This is a "paraffin-base" oil, but contains small quantities of the olefin series C_nH_{2n}, the benzene series C_nH_{2n-6}, and traces of the naphthene series, which are hydrogen addition products of the benzene series, and isomeric with the olefin series. The color by transmitted light varies from amber to red, and by reflected light is green, due to the so-called "bloom" or fluorescence. In specific gravity it ranges generally from .8641 to 7821 (32.0 to 49.0° Beaumé). It contains very little sulphur (.06 to .084), practically no asphaltic matter, and gives a good yield of gasoline, illuminating oils, and paraffin wax.

The Canadian oil and that from Lima, Ohio, are also paraffin-base oils; but as they are high in sulphur (Lima[1] oil 0.6 per cent, and Petrolia, Canada,[1] 0.98 per cent), the illuminating oils separated from them have to be desulphurized in order to make them merchantable.

The petroleum from Illinois is lower in sulphur (.25 per cent to .32 per cent), much of it being refined without special treatment; but that from some pools contains asphalt as well as solid paraffin, as do some from Kansas, Oklahoma, and Northern Texas.

The California[2] oils are of the asphaltic type and are made up of a large proportion of nitrogen bases of the pyridin, or hydropyridian, and chinolin type. They also contain members of the terpene series, C_nH_{2n-4}, and the benzene series, C_nH_{2n-6}, as does the oil from Beaumont, Texas.

There are small quantities of petroleum produced in Pennsylvania, West Virginia, and other localities, which possess lubricating qualities in their natural state, and need only to be strained before they are placed on the market; but, as the production is small, these oils are only of passing interest.

Of the other countries, Russia is the largest producer. The oil from Baku differs chemically from the Pennsylvania oil in being made up largely largely of the "naphthene" series, which, according to Markownikow[3] and Ogloblin, constitutes 80 per cent.

Smaller fields exist in Sumatra, Java, Borneo, Galicia, Roumania, Egypt, Persia, Africa, India, Japan, Mexico, Germany, Peru, and Italy.

The following table gives the rank of the petroleum producing countries, with the quantity produced and the percentage of each in 1908, in barrels of 42 gallons:

[1] Mabery.
[2] Prof. F. W. Bushong, Univ. Kansas Bull. Vol. IX, p. 307.
[3] Jour. Chem. Soc XLII, 390; XLVI, 1276.

WORLD'S PRODUCTION OF CRUDE PETROLEUM, 1908, BY COUNTRIES [1]

(Barrels of 42 gallons.)

	Quantity.	Percentage.	
United States:			
Oklahoma	45,798,765	16.08	
California	44,854,737	15.75	
Illinois	33,685,106	11.84	
Texas	11,206,464	3.94	
Ohio	10,858,797	3.82	
West Virginia	9,523,176	3.34	
Pennsylvania	9,424,325	3.31	
Louisiana	6,835,130	2.40	
Indiana	3,283,629	1.15	
Kansas	1,801,781	.63	63.09
New York	1,160,128	0.41	
Kentucky	727,767	0.26	
Tennessee [1]			
Colorado	379,653	0.15	
Utah	17,775		
Wyoming			
Michigan		0.01	
Missouri	15,246		
Russia	62,186,447	21.85	
Sumatra, Java and Borneo	8,752,822	3.08	
Galicia	12,612,295	4.43	
Roumania	8,252,157	2.90	
India	5,047,038	1.77	
Japan	2,070,929	0.73	
Mexico	3,481,410	1.22	
Canada	527,987	0.19	
Germany	1,009,278	0.35	
Peru	1,011,180	0.36	
Italy [2]	60,000		
Others [2]	30,000	0.03	
		100.00	

[1] No production in Tennessee recorded in 1908. [2] Estimated.

Production. Crude petroleum is obtained by drilling through the overlying strata to the oil producing sands beneath, proceeding in practically the same manner as in boring an artesian water well. The depth of the wells depend on the locality. In Pennsylvania the depth varies from 300 to 3700 [2] ft. It sometimes happens in drilling, when the oil bearing strata is tapped, that the oil rushes out of the well with great force, due to confined gas; such a well is called a "gusher." Some of the big gushing wells of Russia have started producing at the rate of 200,000 barrels of oil per day. The famous Lucas well struck at Spindle Top near Beaumont, Texas, on Jan. 10, 1901, at a depth of from 1029 to

[1] "The Production of Petroleum in 1908," by David T. Day, Dept. of the Interior, U. S. Geological Survey.

[2] "Petroleum and its Products," by Sir Boverton Redwood.

1069[1] ft., is estimated to have started gushing at the rate of 70,000 barrels per day, and probably flowed 500,000 barrels before it could be capped.

Although we are producing more oil now than ever before, owing to the development of new fields, the older fields are slowly diminishing in production. According to the U. S. Geol. Report for 1909, Pennsylvania, in 1891, produced 33,009,236 barrels, and Texas, in 1905, produced

FIG. 268.

28,136,189 barrels; Pennsylvania, in 1908, produced only 10,584,453, and Texas, 11,206,464 barrels.

The production of a well is sometimes increased by "shooting," i.e., by exploding a shell of nitro-glycerine in the producing zone. Photograph, Fig. 268, shows a well spouting after being shot.

As the Pennsylvania petroleum is of excellent quality, it is found profit-

[1] U. S. Geol. Survey Bull. "The Production of Petroleum in 1902," F. H. Oliphant.

able to pump wells yielding only one-fourth barrel per day; such wells are connected in series and worked as a unit.

The petroleum as produced is always accompanied to a greater or less degree by water and B. S. (bottom settlings). The water is removed by settling, and also the B. S., if it is earthy matter, or inert organic matter;

Fig. 269.

but in case of Pennsylvania petroleum, where it is principally an emulsion of amorphous paraffin wax and water, it is refined with the crude oil after the water has been separated.

Petroleum is transported great distances from the fields to the storage tanks (30,000 to 75,000 barrels capacity) of large refineries, through pipe

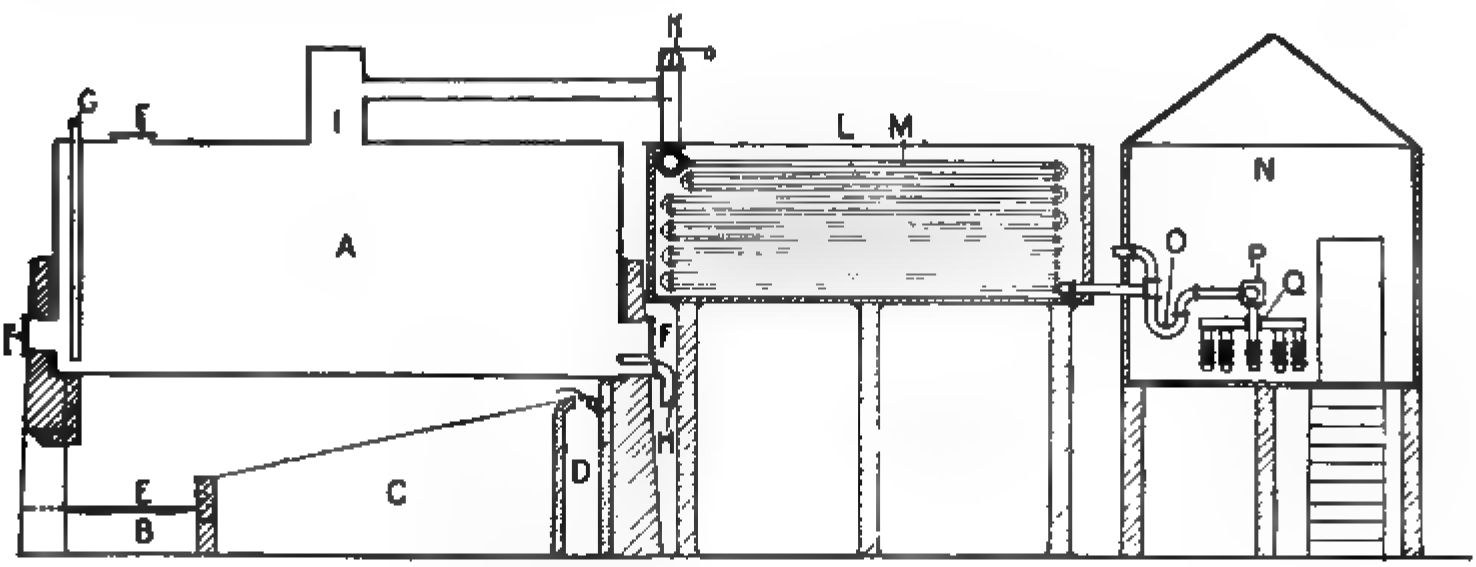


Fig. 270.—*A*. Still; *B*. Ash-pit; *C*. Filling; *D*. Flue; *E*. Fire-box; *F*. Manholes; *G*. Filling line; *H*. Pumping out line; *I*. Dome; *J*. Goose neck; *K*. Safety valve; *L*. Condenser box; *M*. Condenser coil; *N*. Tail house; *O*. Gas trap; *P*. Link box; *Q*. Manifred.

lines of from 4 ins. to 8 ins. in diameter, the average line being 6 ins. The longest distance known to the writer is from the Oklahoma field, via. Kansas City and Chicago, to the seaboard, a distance of about 1600 miles.

Refining. The first step in the separation of petroleum into its various products is fractional distillation, and this is modified according to

the nature of the crude oil, and the products desired. The horizontal steel stills[1] used for this operation vary in construction, but those in gen-

Fig. 271.

eral use in this country[2] are cylindrical steel shells set in brickwork, as shown in Figs. 269 and 270, the upper half being exposed except for an iron jacket covering. The largest stills of this type are about 42 ft. long by 15 ft. in diameter, with a charging capacity of about 1200 (42 gallons) barrels. They may be either end or side fired, the latter being preferable on account of the ease with which the still can be controlled. The fuel used may be either coal or oil, it being cheaper to burn oil in some cases, as in California and Russia, where, owing to the scarcity of coal, oil is used almost entirely.

Fig. 272.

The stills are usually fitted with domes at the top which are connected

[1] Several years ago the "Cheese box" or upright still were used, but proving expensive to operate and to repair they were discontinued.

[2] In Russia and also slightly in this country horizontal stills with longitudinal flues are used.

with 12 to 16-inch vapor pipes, or " goose necks " that lead to condensers. The condensers consist of coils of pipe set in tanks, through which cold water is circulated. The pipes connecting the condenser coils with the " tail house," some distance away, are called the " running lines," and are usually provided with traps for separating the uncondensed gas which accompanies the distillate to a greater or less extent, and which for purposes of economy is utilized in gas engines or burned under the boilers or stills. The running lines are intercepted in the " tail house " by " look boxes " enclosed with glass, Fig. 273, so that the "stream " (distillate flowing from the condenser) can be watched by the stillman in charge. The

FIG. 273.

look time to time. The process is usually controlled by the gravity of the boxes are equipped with small cocks, so that samples can be taken from stream, or other simple tests made by the stillman. The bottom of the " look box " connects with a manifold usually having cocks or valves, so that the distillate may be run into any receiving tank desired.

In some refineries, several stills are connected and run continuously, by simultaneously charging into the first still slowly, and pumping from the last, each still being fired stronger than the preceding one, so that different boiling point fractions are obtained from each one.

When distilling oil continuously the heat from the reduced oil passing from the last still is transferred to the oil being charged into the first still, by passing the hot and cold oil in opposite directions through an exchanger. The exchanger consists of a system of coils arranged in a steel shell; the

hot oil passing through the coils gives up its heat to the cold oil being pumped through the shell to the still.

As before stated, the method of distilling is dependent on the products desired. When petroleum is distilled by means of fire alone, the heavy vapors which condense in the top of the still drop back into the superheated oil, and are thereby partially decomposed. This decomposition, or "cracking," causes oils of lower specific gravity than are normally present to be produced, and is called the "dry," or destructive distillation.

COMPARATIVE TESTS OF THREE DIFFERENT SAMPLES OF CRUDE PETROLEUM, ALSO THE SPECIFIC GRAVITIES, AND COLD TESTS, OF THE FRACTIONS OBTAINED FROM SAME BY DESTRUCTIVE DISTILLATIONS

Color, Sulphur, Specific Gravity	Pennsylvania.	Illinois.	Indian Territory.
	Yellow 0.078% 41.9° Beaumé.	Nearly Black, 0.205% 33.8° Baumé.	Dark Green, 0.283% 37.5° Baumé.
Distillation:	% Bé. Gr. ° F.	% Bé. Gr. ° F.	% Bé. Gr. ° F.
First Fraction,	10.0—70.0 —	10.0—60.5 —	10.0—67.9 —
Second "	10.0—58.8 —	10.0—51.5 —	10.0—56.4 —
Third "	10.0—52.8 —	10.0—45.6 —	10.0—50.6 —
Fourth "	10.0—48.1 —	10.0—40.6 —	10.0—45.1 —
Fifth "	10.0—43.7 —	10.0—36.7 —	10.0—40.5 —
Sixth "	10.0—40.2 28 C.T.	10.0—34.3 36 C.T.	10.0—36.6 41 C.T.
Seventh "	10.0—39.3 48 "	10.0—34.2 50 "	10.0—34.2 42 "
Eighth "	10.0—38.9 57 "	10.0—34.6 53 "	10.0—33.9 55 "
Ninth "	10.0—38.8 61 "	10.0—36.8 46 "	10.0—36.6 47 "
Tenth "	8.5—36.9 55 "	6.0—21.3 47 "	5.0—36.9 46 "
Coke and loss	1.5	4.0	5.0
	100.0	100.0	100.0

This method is used when a large percentage of burning oils is desired. The products when running on Pennsylvania, or paraffin-base crude oil, are: naphtha (sometimes redistilled, for cymogene, rhigolene, petroleum spirit and gasolene), burning oils, gas and fuel oils, paraffin lubricating oils, wax and coke. The usual practice is to first "run" the "crude" to tar (about 9 to 12 per cent residuum) in the crude stills, and to distil the tar separately at the tar stills for paraffin or "tar" distillate (lubricating oil distillate containing the paraffin wax) and coke.

When lubricating oils of superior quality, such as spindle and cylinder oils, are being manufactured, it is necessary to prevent the decomposition of the crude oil as much as possible, and this is accomplished by introducing steam (dry[1] but not necessarily superheated) into the oil in the still by means of a perforated coil. The vapor pressure is lowered by this process, and the hydrocarbons distil over at temperatures lower than their normal boiling points. The steam jets also keep the oil in constant state

[1] In the writer's experience, the "P. J. Heffernan Improved Steam Trap" has proven the most satisfactory for this purpose.

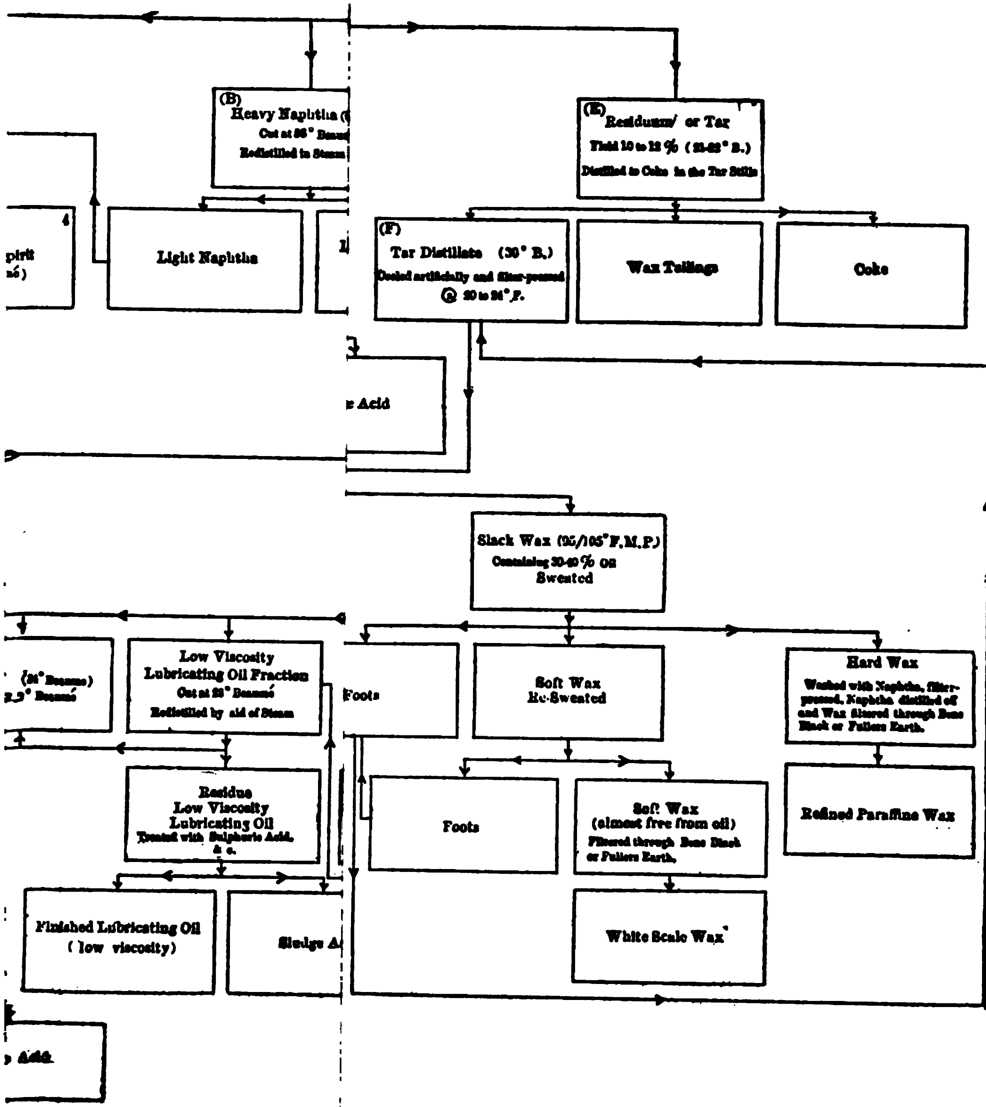
of agitation, thereby preventing it from getting overheated at the bottom of the still next to the fire. This method is called the " steam " distillation; the products are: Naphtha, burning oils (less than when distilled destructively), gas and fuel oils, spindle oils, paraffin wax and cylinder oils. Some refiners use the vacuum distillation, in conjunction with the steam distillation, were, by the aid of a pump, a partial vacuum is created in the still, and the hydrocarbons pass over at temperatures much below their normal boiling points. The vacuum stills are of the same general type as the ordinary horizontal " crude stills," but are smaller and heavier.

Naphtha and Illuminating Oils. The chart on opposite page shows the different steps in the " dry " distillation of Pennsylvania crude oil. The " stream " (distillate flowing from the condenser) begins running into the " tail house " under ordinary conditions at about 80° Bé. (.6666 sp. gr); it is practically water white in color, and is " run " into light naphtha (Fraction *A*) until it reaches 69° Bé. (.6965 sp. gr.). From 69 to 58° Bé. (.7035 to .7446 sp. gr.) the distillate is collected as heavy naphtha (Fraction *B*); but as it is more or less contaminated with some of the heavier hydrocarbons of boiling points too high for use as naphtha, it has to be redistilled in a " steam still," (a still heated by steam coils and steam jets). The upper fraction is added to the light naphtha (Fraction *A*), and the residue used for blending with the low test burning oil which follows.

The naphtha Fractions *A* and *B*, representing from 12 to 15 per cent of the crude oil, can be worked up in several different ways. They can be used for all ordinary purposes without further refining, or may be redistilled, the very volatile fractions being condensed by exterme cold, and under pressure, thereby separating cymogene, rhigolene, gasolene and petroleum spirit, which Allen in his " Commercial Organic Analysis," Vol. II, part I, p. 96, classifies as follows:

Commercial Name.		Degrees Baumé.	Specific Gravity.	Composition.
Cymogene		108	0.588	Consists chiefly of tetrane, C_4H_{10}.
Petroleum Ether	Rhigolene	94 to 92	0.625 to 0.631	Consists chiefly of pentane and isopentane, C_5H_{12}.
	Gasolene (Canadol)	95 to 80	0.622 to 0.666	Consists chiefly of hexane, C_6H_{14} and isohexane.
Petroleum Spirit or Benzolin	C. Naphtha, Benzine-naphtha	76 to 70	0.680 to 0.700	
	B. Naphtha	66 to 65	0.714 to 0.718	
	A. Naphtha	59 to 58	0.740 to 0.745	
	Benzin			

In order to improve the odor of the naphtha it is sometimes treated with about two to four pounds of 66° Bé. commercial sulphuric acid per



PRODUCTS OBTAIND AUBERT. *(To face Page 510.)*

barrel of 50 gallons, by agitation in tall, lead-lined cone-bottomed tanks, Figs. 274 and 275, called agitators, of from 300 to 500 barrels capacity, provided with mechanical stirring gears, in preference to an air blast, in order to prevent loss by evaporation. The acid is allowed to settle and draw off into the sludge acid tank. The naphtha is washed thoroughly with water by means of a spray and finally by agitation with water, and is then made alkaline with caustic soda of 4 to 10° Bé., and finally washed with water until neutral, when it is pumped into tanks and allowed to settle until bright. After this treatment it becomes known as "deodorized naphtha."

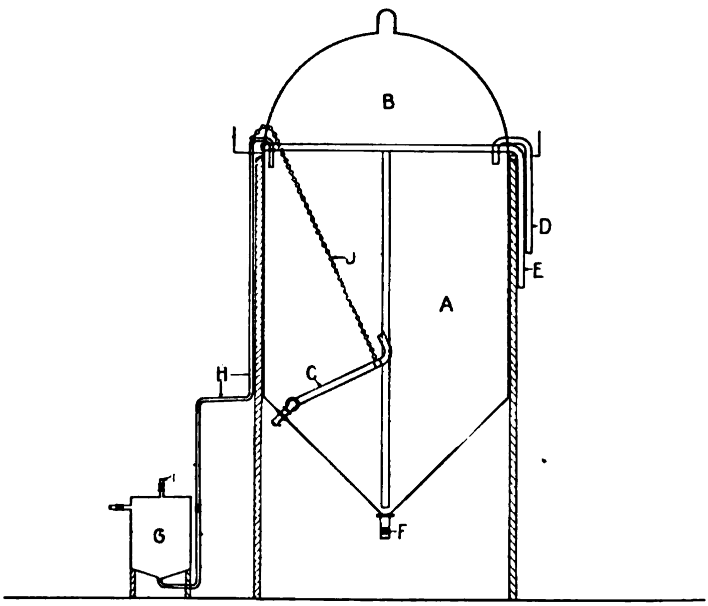


FIG. 274.—*A*. Agitator; *B*. Dome; *C*. Swing suction for pumping out oil; *D*. Oil-filling line; *E*. Air blast; *F*. Cock for drawing off sludge; *G*. Acid tank; *H*. Acid line; *I*. Compressed air line; *J*. Chain for operating swing suction.

To recur to the original distillation, from 58 to 43° (.7446 to .8092 sp. gr.), or as long as the stream runs good color (almost colorless) the high test burning oil (Fraction *C*), is collected. It is "steam stilled" to 150° F. fire test, and the distillate put into heavy naphtha (Fraction *B*). The residue from the steam, still known as 150° W. W. Stock, is treated as described later.

When the distillate begins to go "off color," due to cracking, it is "cut into" low flash burning oil distillate (Fraction *D*), which is also steam stilled, the volatile fraction being naphtha of 70° Bé. (.7000 sp. gr.), called "gas naphtha" from its objectionable odor. Gas naphtha contains a large proportion of unsaturated hydrocarbons, and goes into the cheaper

grades of naphtha. The appearance of so low a specific gravity fraction at this stage of the distillation, illustrates clearly the effect of the "cracking" process.

The burning oil stocks from the steam stills, constituting from 65 to 75 per cent of the crude oil charged, are treated at the rate of 5 to 10 lbs. of 66° commercial sulphuric acid per barrel, in order to improve the color and odor, also to remove decomposition products which cause the flame to smoke when burned in lamps. The process is performed in agitators in much the same manner as with naphtha, only an air blast is used for agitation instead of a stirring gear. In order to get the full benefit of the acid, any water present must first be drawn off, and a small

Fig. 275.

amount of acid added in order to remove all of the remaining water; this is agitated for from 20 to 40 minutes, allowed to settle from the oil and then drawn off. The remaining acid is then added and the mass agitated for from one-half to one hour, allowed to settle from 3 to 5 hours, and drawn off. The acid treatment removes the tarry matter formed during distillation, also a large percentage of the unsaturated hydrocarbons and sulphur compounds. The acid is turned almost black after treatment, and is known as "sludge" acid. The "sludge" acid is allowed to settle from the oil and is then drawn off into tanks and delivered to the acid separating plant for the recovery of the acid, which will be described later. After the separation of the sludge, the oil is washed thoroughly with water, made alkaline with caustic soda of from 4 to 10° Bé. by agitation, and then washed with water until neutral;

the wash water is separated and the oil pumped into settling tanks where it is allowed to settle until bright.

Sulphur Content. Pennsylvania petroleum contains very little sulphur (.06 to .082 per cent), the burning oils made from it therefore requiring no further treatment; but when oils containing considerable sulphur, such as that from Lima, Ohio, Texas, and Canada, are being refined a special desulphurizing is necessary in order to get rid of most of the sulphur compounds which cause charring of the lamp wick, and burn with a smoky flame. There are many processes for affecting this, the two best known being the "litharge" and the "Frasch" methods.

The litharge method consists of agitating the oil with a solution of litharge (lead oxide) in caustic soda; the sulphur is precipitated as a lead sulphide and drawn off. Although this method reduces the sulphur considerably, it is not as thorough as the "Frasch" process, where the oil is heated with finely divided copper, or copper oxide in "sweetening" stills provided with heavy stirring gears. The copper sulphide formed is afterwards roasted in order to remove the sulphur and the resulting copper oxide used for the next treatment.

The residue (*E*) from the original distillation of the crude oil (10 to 12 per cent) is known as tar. It is from 21 to 22° Bé., very dark in color and contains the paraffin lubricating oil and wax.

Lubricating Oils. In order to manufacture the lubricating oils known in the trade as "paraffin oils," the tar is first distilled destructively in stills of practically the same type as the "crude stills," only they are smaller in capacity (250 to 500 barrels). The process is continued until everything has passed over except the coke formed by the destructive distillation. At the latter part of the distillation, just before the still has "coked," a yellow, sticky, semi-asphaltic product passes over which is known as "wax tailings;" on analysis this has been found to contain anthracene, chrysene, and other products formed by the "cracking" process. The bottoms of the stills often get red hot during the coking period. The coke resembles gas coke in appearance, but is more fragile. The yield from tar averages from 10 to 12 per cent, or about 1 per cent from the crude oil, and on account of its purity is used principally for making electric light and battery carbons, and also to some extent in metallurgical processes.

The distillate from tar known as paraffin, or unpressed tar distillate (Fraction *F*), is yellow in color and contains the wax and paraffin lubricating oils. It has a gravity of 30° Bé. (.875 sp. gr.), and a solidifying point of about 70° F. due to the solid paraffins present. It is treated with 66° Be. commercial sulphuric acid at the rate of 8 to 10 lbs. per barrel in the same manner as the treating of burning oils, the agitator in this case being heated by a steam jacket in order to keep the paraffin distillate liquid. After treatment it is delivered to the pressing plant, where it is chilled down to from 20° to 24° F. in steel shells containing stirring gears called "coolers" provided with jackets through which cold

brine is circulated. A refrigerating plant is therefore necessary when refining crude oils containing solid paraffins. When the proper temperature (20° to 24° F.) is reached, it is pumped to a filter press, Fig. 276, which is provided with plates covered with canvas; the oil passes through and drains off, and the wax is held by the canvas. The oil thus expressed is known as pressed tar distillate (Fraction *G*), and the wax separated, containing considerable oil (30 to 40 per cent), known as "slack wax," is removed from the canvas covered plates,[1] by scraping with "spuds," when it is carried by means of conveyors under the press to the "slack wax" tank.

The pressed tar distillate has a cold test (solidifying point) of 20° to 25° F., and is used for making all of the paraffin lubricating oils. It is charged into the "reducing stills," which are the same type as the crude stills, but smaller in capacity (about 300 to 500 barrels); and the upper halves, instead of being exposed, are bricked in. Here it is "steam reduced" according to the test desired, by firing underneath and at the same time introducing steam into the body of the oil by means of a perforated coil placed inside on the bottom of the still. In making high viscosity oils the distillation would naturally be carried further than when making low viscosity oils—as the viscosity increases with the boiling point in the same homologous series of hydrocarbons. The first fraction, separated at 36° Bé. (.8433 sp. gr.), is put into the low test burning oil fraction; the second fraction down to 32.5° Bé. (.8615 sp. gr.), being too high in specific gravity for burning oils, and having practically no value as lubricating oil, is separated for "fuel oil." The third fraction, cut at 28° Bé. (.886 sp. gr.), is used for making low viscosity lubricating oils, as described by chart, and the fourth for medium lubricating oils. The residue, which is heavy lubricating oil stock of dark color, is pumped out of the still through a coil of cast-iron pipe set in water called a cooler, in order to prevent oxidation when exposed to the air. The cool oil is treated with from 20 to 50 lbs. of commercial 66° Bé.[2] sulphuric acid per barrel in an agitator of from 200 to 1000 barrels capacity in the same manner as described under burning oils, except that the agitation is kept on longer—one to two hours—and it takes longer for the sludge acid to settle—four to six hours. Fig. 277 shows the sludge being drawn from a 500 barrel agitator. The amount of acid used in treating depends on the color desired on the finished oil.

After drawing off the sludge, the oil is transferred to a "lye" agitator, where most of the remaining acid is washed out by agitation with water. It is then agitated with caustic soda of from 1 to 6° Bé. until a distinct alkaline reaction with phenolphthalein is obtained. The "lye" containing sulpho-compounds, formed by the acid treatment, is drawn off,

[1] The canvas covers of the plates are usually spoken of as "bags," although the term seems misleading.

[2] Beaumé scale for liquids heavier than water.

FIG. 276.

and the oil washed well again with water, and finally with hot water, until a neutral reaction is obtained. The water is separated and the oil transferred to shallow tanks, where it is warmed to 150° to 160° F. by closed steam coils, and air blown up through it from a perforated coil until all the moisture is removed, leaving the oil clear and bright and ready for the market.

The "sludge" acid from the lubricating oils is black, asphaltic in nature, and very viscous, almost a solid mass. It, with the sludge from the burning oils, is agitated with water in a lead-lined separator; the weak acid recovered is concentrated in lead pans and finally in stills

Fig. 277.

of cast iron to 66° Bé. and is then used over again. The residue is used for fuel, or worked into pitch.

Paraffin Wax. The slack wax expressed from the tar distillate usually contains from 30 to 40 per cent of oil, which is gotten rid of by one of the following methods: it may be mixed with naphtha and cooled until the wax crystalizes out, and then refilter pressed; or it may be removed by the process known as sweating. The "sweaters" consist of tiers of pans arranged in rooms, as shown in Fig. 278; the rooms are heated by steam coils, each room being known as an oven. The pans are first filled with water to the level of a wire screen at *A* and the melted wax is charged in until the pans are full, after which cold water is circulated through coil *B* until the wax solidifies. The water is then drawn off from underneath the solid cakes of wax by valve *C* and warm water circulated through coil *B* and the rooms also heated by steam coils. The heat

causes the oil to sweat out of the wax, and it drains off and runs into a tank. The oil, or "foots," thus separated, containing some soft wax, is filter pressed and worked up the same as the unpressed tar distillate. The sweated wax remaining in the pans is melted, drawn off, and delivered to the filtering plant, where it passes through bone black or fuller's earth contained in long cylindrical tanks called filters in rooms heated from 130° to 180° F. This operation removes practically all of the color. It is then molded into cakes either in pans or between hollow plates cooled by the circulation of water in apparatus shown in Fig. 279, known as the "Gray Wax Caking Machine."[1]

FIG. 278.

The Steam Distillation. Spindle oils and cylinder stocks. In making special high-grade lubricating oils, the distillation of the crude oil is carried on in the same manner as the destructive distillation until just before the "cracking" point is reached, when steam is introduced as before mentioned; by this method decomposition is practically prevented. The yield of burning oil is therefore much lower and lubricating oil much higher. The distillation is carried on until about 15 to 18 per cent remains in the still. The reduced stock, known as steam refined cylinder stock, is pumped out through a cooler.

The steam refined cylinder stocks are sometimes further refined by

[1] Patented by A. McD. Gray (built by S. L. Moore & Sons of Elizabeth, N. J.).

filtration through bone black or fuller's earth and are then known as filtered cylinder oils. Cylinder oils [1] are recognized by their high flash point and viscosity.

After the burning oil fraction has been separated, the rest of the distillate, passing over during the distillation, is called "spindle distillate." It contains considerable wax, which is removed by filter pressing in exactly the same manner as with the unpressed tar distillate. The pressed spindle distillate is reduced in the same manner as the paraffin oils, except that the reduced spindle oil stock, instead of being treated with acid is filtered through bone black, or fuller's earth, contained in cylindrical filters of about 15 to 20 tons capacity. The fuller's earth removes the asphaltic matter, and improves the color of the oil. The first oil running through the filter is almost colorless; but as the fuller's

Fig. 279.

earth "adsorbs" the asphaltic matter, it soon loses in decolorizing value and the oil runs darker until it reaches a point where it is not practical to filter any longer, when the operation is stopped. The oil held by the fuller's earth is washed out by allowing naphtha to filter through it, and the naphtha remaining in the filter is collected by steaming it out with an open steam jet, and running it through a condenser. The oil washed out by the naphtha is separated by distillation, and the fuller's earth is heated in a retort nearly to redness in order to dry it and burn off the asphaltic matter, when it is used over again.

Vaseline and "petrolatum" are reduced stocks made from selected crude oil by careful reduction and subsequent filtration through fuller's earth, or bone black.

[1] The problem of the lubrication of gas engine cylinders has created a new class of cylinder oils, which are made from the steam distillate (heavy distillate), from steam distillation and are of lower viscosity and fire test.

Asphaltic Base Crude Petroleum. The refining of asphaltic base crude oil is substantially the same as described in the preceding methods, excepting the residue, which, instead of being tar, or cylinder stock, is asphalt. The burning oils are not of such good quality, a larger percentage of fuel oil is obtained, and the lubricating oils are of higher specific gravity and lower flash than those made from the paraffin base petroleum.

Natural Gas. Although natural gas always accompanies crude petroleum, it is often found independently. It consists principally of gaseous members of the paraffin series, of hydrocarbons, but contains small percentages of olefins,[1] nitrogen, carbon dioxide, and sometimes oxygen and hydrogen.

Natural gas is used principally for illuminating and fuel purposes, also to some extent in the manufacture of lampblack.

Shale Oil. In Scotland, and to a small extent in other countries, paraffin oils are obtained by the destructive distillation of bituminous shale. The formation of the oil is dependent on the decomposition of the organic matter present.

Shale varies in color from dark gray to almost black, the products obtained being ammonia water (separated as a sulphate), paraffin wax, paraffin oils, burning oils, and phenols. The shale is first reduced to very small pieces, and then distilled continuously in circular vertical retorts, by charging in the top through a hopper, and drawing the exhausted shale out at the bottom. Steam is usually introduced into the retort. The vapors pass through a condenser, and the crude shale oil and ammonia liquor are separated. The remaining gases are subjected to a scrubbing process which consists of passing the gas through coke towers, where it comes in contact with streams of oil and water; the oil absorbs a large portion of the hydrocarbons, and the water takes up the ammonia, the residual gas being used for fuel. The compression process has also been used for condensing the gases; by this process the gas is subjected to low temperatures, and under a pressure of from 75 to 150 lbs. per square inch, but this method is said to be more expensive than the process of scrubbing. The crude shale oil [2] is dark in color, ranging in specific gravity from .86 to .89, and having a cold test of 90° F. due to solid paraffins. It is distilled by either the intermittent or continuous process to coke in practically the same manner as with the tar from crude petroleum, except that steam is introduced through perforated coils during the distillation process. The treatment of the various fractions i.e., naphtha, burning oil, paraffin distillate (containing the paraffin wax)— consists of a treatment with sulphuric acid and alkali in the same manner as with petroleum; the alkali in this case, in addition to neutralizing the acid, removes the phenols which have been formed during the first

[1] University Geol. Survey of Kansas, Vol. IX.

[2] Redwood, "Petroleum and its Products."

distillation. The phenols are liberated[1] from the waste "lye" by passing carbon dioxide through it.

Ozokerite. Ozokerite, or earth wax, is, as the name implies, a wax-like substance found in small quantities throughout the world, usually associated with rock salt or gypsum. The principal deposit occurs in the neighborhood of Boryslaw, in Galicia. It consists largely of solid paraffin hydrocarbons, and is supposed to have resulted from the evaporation and decomposition of crude petroleum. Like petroleum, it is found in different ages, but principally in the Tertiary and the Cretaceous. The appearance and physical character vary, some grades being soft and others brittle, and the color ranges from yellow to black. The specific gravity averages from .85 to .89 and the melting point[2] from 130° to 156° C. The Galician ozokerite is mined by sinking a shaft and then following the vein. Thus mined, it often contains much earthy matter. The purest pieces are first separated by hand picking, and the remainder is dumped into tanks of cold water; the purer ozokerite rises to the surface and is skimmed off, and the earthy matter, containing some ozokerite, sinks to the bottom. This residue is then heated in boiling water, when practically all of the ozokerite rises to the surface and is separated. The earth is finally extracted with naphtha, thereby dissolving the last traces of ozokerite. Ceresin, or refined ozokerite, is used largely as a substitute for beeswax, and is prepared by treating with sulphuric acid, washing with water, and neutralizing with caustic soda, as described under petroleum refining, and subsequent filtration through bone-black or fuller's earth. It varies in color from white to yellow, according to the degree of refining. Ozokerite is sometimes distilled and worked up for paraffin wax.

Asphalt. The name asphalt is generally applied to that class of bitumens found naturally in the earth in various parts of the world. It consists principally of compounds of carbon and hydrogen, also compounds containing nitrogen, oxygen, and sulphur and some mineral matter, and is considered to have resulted from crude petroleum. Asphalt is black in color, and melts easily on the application of heat. It is partly soluble in petroleum spirit and completely soluble in carbon disulphide, the part soluble in petroleum spirit being designated "petrolene," and the part soluble in carbon disulphide, "asphaltene." The principal uses are for street paving, weather-proofing, paints and japans. The most important production is from "Pitch Lake," on the island of Trinidad, which is 135[3] feet deep at the center and originally covered an area of approximately 127 acres, and is estimated to contain several million tons of asphalt.

[1] "Mineral Oils and their By-products," I. I. Redwood.

[2] Redwood, "Petroleum and its Products."

[3] Report of the Inspector of Asphalt and Cements. Eng. Dept. District of Columbia, 1892.

The crude lake asphalt, according to Clifford Richardson,[1] contains the following constituents:

Water and gas	29.0%
Organic matter not bitumen	7.0
Mineral matter	25.0
Bitumen	39.0
	100.0%

The method of refining consists of melting and removing the mineral matter which subsides. The composition of the refined Trinidad Lake Asphalt is given as follows:

Bitumen (soluble in carbon disulphide)	56.4%
Organic matter, not bitumen	6.7
Mineral matter	36.9
	100.0%

The asphalt residues from crude petroleum so closely resemble the natural asphalts that they cannot be distinguished with certainty. Petroleum asphalts are used principally for weather-proofing.

Other deposits occur in California, Utah, Mexico, Venezuela, Cuba, France, Switzerland, and Germany.

Method of Testing

Crude Petroleum. The New York Produce Exchange defines crude petroleum as follows: "Crude petroleum shall be understood to be a pure natural oil, neither steamed nor treated, free from water, sediment, or other adulteration, of the gravity of 43° to 48° Bé." Since the production of the lower Baumé gravity oils, the limitations in regard to gravity have been relaxed.

In order to ascertain whether or not the petroleum conforms to the above rule, it is distilled in 10 per cent fractions, and the Baumé gravity determined on each fraction. It is obvious that, from the complexity of crude petroleum, each succeeding fraction would show a somewhat regular gradation in specific gravity, whereas, in cases of adulteration, it would be more or less irregular.

In order to ascertain the commercial value of crude petroleum, Dr. Engler recommends the distillation of 100 c.c. from a distillation flask of the dimensions in cubic centimeters shown in Fig. 280. The distillation is controlled so that from 2 to 2½ c.c. of distillate pass over per minute, heat being applied by means of a Bunsen burner. At the beginning of the distillation a piece of wire gauze is interposed between the flame

[1] "The Modern Asphalt Pavement," C. Richardson.

and the flask, but finally the naked flame is used. As soon as the temperature reaches 150° C., the burner is removed until the temperature falls 20°. It is then reheated to 150° C., and the cooling and heating process continued until no more distillate passes over. This fraction is classed as naphtha. The distillation is then continued until 300° C.[1] is reached, when the temperature is allowed to drop as before. This fraction is separated as illuminating oil, the residue representing the lubricating oil.

In Dr. Ubbelohde's modification of the Engler method, the condenser tube is bent vertical at the end farthest from the flask in order to drop the distillate into one or another of a series of graduated test tubes contained in a holder. The temperature at which the first drop of distillate runs into the test tube is taken as the beginning of boiling. The distillation is then continued at two drops per second up to 300° C., the fraction up to 150° C. being taken as naphtha, and from 150 to 300° C. as burning oil.

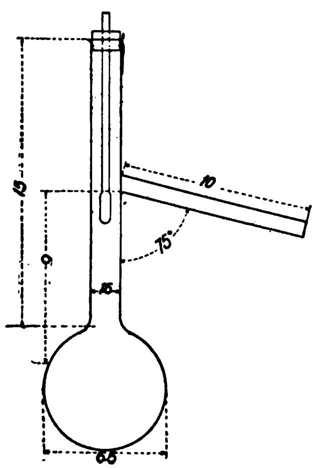


Fig. 280.

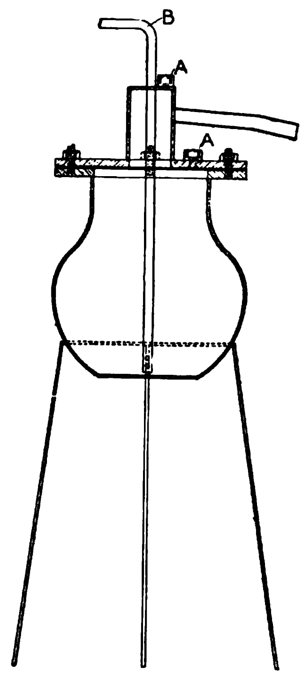


Fig. 281.

In order to determine roughly the yield of products likely to be obtained in actual refining, the author recommends the distillation of from two to four liters of the crude oil. A convenient form of still is shown in Fig. 281. The distillation is carried to coke and controlled so that from 5 to 10 c.c. of distillate pass over per minute, it being separated in one per cent fractions, and the Baume gravity determined on each fraction. All of the fractions over 58° Bé. are added together for the naphtha frac-

[1] When distilling petroleum made up largely of the naphthene hydrocarbons, the burning oil is separated at 285° C. instead of 300° C.

tion, those between 58° and 36° Bé. for the burning oils, and the distillate passing over, below 36° as lubricating distillate, the residue being coke.

Sulphur. Since the illuminating oils made from crude petroleum of high sulphur content require special treatment, it is desirable, in estimating the value of crude petroleum, to know the percentage of sulphur it carries. The method of Mr. C. I. Robinson is the quickest and simplest method known to the writer. It is described [1] as follows: "(1) A dilute aqueous solution of tropæolin, 00. (2) A solution of sulphuric acid, 1 c.c equal to 0.001 grams of sulphur. (3) A solution of sodium carbonate equivalent to the sulphuric acid. About 5 or 6 c.c. of the oil to be examined are poured into the Erlenmeyer flask *A*, Fig. 282, which is about 15 or 20 c.c. capacity, and contains a wick passed through a glass tube which is held in place by a cork. The flask with the wick is then weighed, the second decimal place being sufficiently accurate. It is then placed under the small tube *C*, which is connected with the absorption apparatus *D*, one limb of which contains glass beads,[2] and into which 5 c.c. of the standard alkali solution has been run. *D* is connected with suction. When the apparatus is all in place, the suction is turned on, and the wick *B* is lighted. The suction draws all the products of combustion through *D*. The *S* contained in the oil is all burned to SO_2 and SO_3, and is absorbed by the sodium carbonate solution. The oil is allowed to burn about thirty minutes—until 2 or 3 grams are consumed. The tube *C* is rinsed into *D*, a few drops of tropæolin added, and the excess of sodium carbonate titrated with the standard sulphuric acid, and the amount of sulphur calculated."

FIG. 282.

Specific Gravity. The Baumé hydrometer is in general commercial use in this country for determining the "gravity;" but, in cases where extreme accuracy is required, the pyknometer should be used. The Westphal balance is sometimes found convenient to use instead of the hydrometer.

Water and B. S. are determined by mixing the crude petroleum with naphtha, half and half, in a 100 c.c. cylinder tapered at the bottom and graduated in tenths, and allowing the mixture to stand for twenty-four hours. The water and B. S. settle to the bottom, and are reported collectively. A centrifuge is sometimes used for forcing the separation.

Illuminating Oils. The specific gravity and sulphur are determined as in the case of crude oils.

Color. Redwood recommends the use of Stammer's chromometer,

[1] The rapid method for the estimation of sulphur in crude petroleum and illuminating oils, Proc. Va. Chemists Club, Vol. I, p. 53, 1908. C. A., Vol. III, p. 115, and Vol. III, p. 2627.

[2] Mr. Robinson advises using broken glass rods instead of beads, the latter being usually made of soft glass so soluble in water as to increase the alkalinity of the solution to the extent of rendering the determination worthless.

which consists of two cylinders closed at the ends with glass. By means of a mirror, light is reflected upward through the cylinders, and the optical arrangement at the top contains prisms allowing both columns to be observed through one eye piece on a circular field divided in the center. The graduated cylinder is filled with oil to be tested, and a glass disk of standard color interposed between the mirror and the eye piece of the other cylinder. The wheel lowers the small cylinders until the divisions on the field of the eye piece are of the same color. The color of the different grades of burning oils on the market are as follows:

Water white		
Standard white	40	Stammer's chromometer
Prime white	50	"
Superfine white	190	"

Flashing Point and Fire Test. The instruments used for these tests are of two types—viz., the open and closed cups. The Tagliabue and Saybolt open cups and the Abel closed cup are among those generally used. The Tagliabue cup consists of a glass cup supported in a copper bath, and heated by a spirit lamp. The cup is filled with the oil to be tested, a thermometer placed in it so that the bulb is covered, and the oil heated slowly, the flashing point being determined by passing a small flame over the surface of the oil until the vapor given off flashes momentarily. The heating is then continued until the oil ignites and burns, which temperature is taken as the fire test.

The Saybolt electric tester, which has been adopted by the New York Produce Exchange, is of similar construction, but the flash is tested by passing a spark from an induction coil between two platinum wires placed over the oil. The water is heated to 100° F., then the flame removed and the cup filled with oil and placed in the bath. A spark is passed for every rise of one degree, and when the oil has reached 90° F. it is necessary to heat again. After the oil has flashed, the sparks are passed at temperatures as follows: "In 110 (fire test) and upwards the flashing point after the first flash (which generally occur between 90° and 95°) shall be taken at 95°, 100°, 104°, 108°, 110°, 112°, 115°. In a 120° and upwards, after the first flash, 100°, 105°, 110°, 115°, 118°, 122°, 125°. In a 130° and upwards every 5° until the burning point is reached."

The open test method is affected by drafts, and is variable. For this reason the closed test cup was introduced.

The Abel apparatus, adopted by England, is described in the petroleum act of August 11th, 1879, as follows: "The oil cup consists of a cylindrical vessel 2 ins. in diameter, 2.2 ins. in height, (internal), with outward projecting rim 0.5 in. wide, $\frac{3}{8}$ in. from the top, and $1\frac{7}{8}$ ins. from the bottom of the cup. It is made of gunmetal or brass 17 B.W.G., tinned inside. A bracket, consisting of a short, stout piece of

wire bent upwards and terminating in a point, is fixed to the inside of the cup to serve as a gauge. The distance of the point from the bottom of the cup is 1½ ins. The cup is provided with a close-fitting, overlapping cover, made of brass (22 B.W.G.), which carries a thermometer and test lamp. The latter is suspended from two supports by means of trunnions, upon which it may be made to oscillate; it is provided with a spout, the mouth of which is $\frac{1}{16}$ in. diameter. The socket which is to hold the thermometer is fixed at such an angle, and its length is so adjusted, that the bulb of the thermometer, when inserted to its full depth, shall be 1½ ins. below the center of the lid."

"The cover is provided with three square holes, one in the center, 0.5 ins. by 0.4 ins., two smaller ones, 0.3 ins. by 0.2 ins., closed to the sides and opposite to each other. These holes may be closed and uncovered by means of a slide moving in grooves and having perforations corresponding to those on the lid. In moving the slide so as to uncover the holes, the oscillating lamp is caught by a pin fixed in the slide and tilted in such a way as to bring the end of the spout just below the surface of the lid. Upon the slide being pushed back so as to cover the holes, the lamp returns to its original position. Upon the cover, in front of and in line with the mouth of the lamp, is fixed a white bead, the dimensions of which represent the size of the test flame to be used."

"The heating vessel or water bath is filled by pouring water into the funnel until it begins to flow out of the spout of the vessel. The temperature of the water at the commencement of the test is to be 130° F. The bath, having been raised to the proper temperature, the oil to be tested is introduced into the petroleum cup, being poured slowly until the level of the liquid just reaches the point of the gauge fixed in the cup. The results obtained with this cup show on the average about 27° F. lower than the open cup. Details of the operation of the instrument are given by Redwood in "Petroleum and its Products," Vol. II.

Lamp Tests. The usual practice is to burn samples of the oil in lamps of ordinary construction for from five to twenty-four hours, observing the diminution of the flame and the incrustation of the wick.

Lubricating Oils. In this country the fire test is generally determined by means of the Cleveland cup. The method is substantially the same as with the burning oils, with the exception that the oil is heated at the rate of 10° per minute, and the flashing point tested with a small bead flame for every rise of 5°. The fire test is, as a rule, from 60 to 80° higher than the flash point. As the open cup tests are easily affected by drafts, they are subject to errors of 5°.

Closed Test. The Pensky-Martin cup is generally used for this test. It is similar in construction to the Abel cup, and contains a stirring apparatus by means of which a uniform temperature of the oil may be obtained. The results obtained by this instrument are, as a rule, close to those obtained by the open cup, but are not subject to errors of the open cup.

Cold Test (Setting Point). As the solid paraffins are poor lubricants, oils of low cold test are desirable. The method commonly used may be described briefly as follows: In an ordinary 4-oz. sample bottle, about one-third full of the oil to be tested, the bulb of a thermometer, which passes through a cork in the neck of the bottle, is just immersed in the oil. The sample is cooled slowly to 50° F. and then subjected to a freezing mixture of ice and salt. The bottle is removed for every few degrees drop in temperature and tilted to see if the oil is still liquid, the temperature at which it just ceases to flow being taken as the cold test or setting point. If the conditions of this method are carefully followed, the results should check within 1° or 2°. In the case of reduced stocks which have not been treated either by acid or filtration through fuller's earth or boneblack, the cold test is unreliable, as the tarry matter present in these oils seems to hold the wax in solution. For illustration, some reduced stocks which show a cold test of 30° F. before filtration through fuller's earth or boneblack are solid at ordinary temperature after filtration. In the case of oils having cold tests higher than 45° F. it is customary to reverse the process—that is, freezing the sample solid, first, to about 20° F. lower than the point at which it congeals, and then gradually warming in water until on tilting it shows a perceptible flow.

Color. The color determination of lubricating oils is not only important as a matter of convenience in keeping records, but indicates the degree of refining the oil has received. For this purpose the Lovibond tintometer is to be recommended. This instrument is made of wood and divided longitudinally by a partition, one side to be used for the sample and the other side, which is slotted, for the standardized colored glasses. The oil, depending upon the depth of color, is tested in cells from ½ in. to 12 ins. long. Very dark red oils, for instance, are tested in ½ in. cells, the lighter color red oils in 2 ins., and pale oils in 6 ins. or even 12 ins. cells. The cell, filled with oil, is placed on one side of the partition, and the standard glasses in the slot of the other side until the color is matched.

Odor. The odor of lubricating oils should be what is known in the trade as "sweet."

Viscosity. The viscosity or internal friction, sometimes expressed as the "body" or "fluidity," although an arbitrary test, is an important one in selecting a satisfactory lubricant. The instruments principally used for making this test are of the same general type, and are known as efflux viscosimeters, the main difference between the instruments being in the dimensions of the capillary through which the oil runs and the amount of oil used for the test. Oils of low viscosity, as, for example, those of the engine, machine, and spindle oil classes, are usually tested at temperatures ranging from 60° to 100° F., and cylinder and other high viscosity oils at 210° to 212° F. The principal instruments of this type are the Engler, Redwood, Saybolt, Tagliabue, and Universal.

The Engler viscosimeter, used in Germany and also to a consider-

able extent in this and other countries, consists of a reservoir *A*, for the oil, enclosed by cover *A*, set in bath *B*. The capillary tube *a* is stopped by plug *b*; 240 c.c of the oil to be tested are poured into the reservoir, and should be just on a level with the points of the studs *cc*. The time required for the delivery of 200 c.c. of distilled water at 20° C. from a charge of 24° c.c. should be from 51 to 53 seconds. The temperature is regulated by means of a ring burner placed under the oil bath. When the proper temperature has been attained, the plug is withdrawn and the outflow of 200 c.c. timed by a stop watch. The time in seconds required for the oil, divided by the time in seconds for water at 200° C., is taken as the "specific viscosity."

The results obtained by the Redwood[1] instrument are compared with rape oil as follows: The time in seconds required for the outflow of 50 c.c. of the oil at 60° F. is multiplied by 100 and divided by 535, which is the average number of seconds required for rape oil under the same conditions. The result is multiplied by the specific gravity of the oil and divided by 0.915, the specific gravity of rape oil.

The Tagliabue, Saybolt and Universal instruments are arbitrary, the results being expressed in seconds for the efflux of about 60 c.c. of the oil.

Paraffin Wax. *Melting Point.* The "English test," which is in reality the solidifying point, is determined by stirring the melted wax in a small cup about 2½ ins. in diameter by about 2 ins. deep until the latent heat given up by the crystallization of the wax arrests the fall of the mercury column momentarily. The "American test" gives results about 3° F. higher than the English test, and is determined as follows: A hemispherical cup 3¾ ins. in diameter is three-quarters filled with melted wax, which is allowed to cool without stirring until a thin film forms on the top, and extends from the sides to a thermometer with a round bulb ½ in. in diameter, suspended so that it is three-quarters immersed in the center of the cup. As the American method is slow, it is customary to take the English test and add 3° F. for the American.

Color. This is determined by the Lovibond instrument, using cells from 6 ins. to 24 ins. in length, the wax being melted. As with the oils, it shows the degree of refining.

Odor and Taste. The odor and taste must be absolutely sweet in the case of refined wax, but the semi-refined waxes usually have a slight odor and taste of light oil.

Per Cent of Oil. The determination of oil in scale and slack wax is determined by pressing a 500-grain sample, at a temperature of 60° F., between pieces of muslin cut to fit the test cup. The oil is absorbed by pieces of blotting paper placed above and below the cloth containing the wax in the test cup.

The cup and plunger are cooled in water to 60° F. before putting in the sample of wax, which has also been cooled to 60° F. The lever press,

[1] Described in "Petroleum and its Products."

Fig. 283, built by the S. L. Moore & Sons Corp. of Elizabeth, N. J., is the one in general use in this country. The test cup and plunger are $5\frac{5}{8}$ ins. in diameter, and a pressure of nine tons on the total surface is applied for five minutes.

Asphalt. *Ball and Ring Method.* A number of methods are in use for the determination of the so-called "melting point." Products of this class, however, on account of their complex nature, do not have a true melting point. The methods in general use are as follows:

Melting Point. "A $\frac{1}{4}$ in. deep by $\frac{5}{8}$ in. diameter ring should be level full of solid asphalt, with some adhering to the top and bottom. This can be done best by filling the ring rounding full with asphalt, cooling in cold water for a few minutes, and then cutting off the excess with a hot knife. There must be no air bubbles inside the ring. A $\frac{3}{8}$-in. steel bicycle ball, weighing about 5 grams, is then placed in the center of the asphalt and the ring hung on a level with the mercury bulb of a thermometer, the point immersed in a beaker of water. For asphalts melting below 100° F. the water should be about 40° F. at the start; for asphalts melting below 150° F., 60–70° F.; for asphalt melting above 150° F., not more than 80° F. The water and beaker should be heated 10° F. per minute, and should not vary more than 1° F. The melting point is the temperature where the ball and pitch begin to drop rapidly on leaving the ring, which is usually about $\frac{1}{2}$ in. below the bottom of the ring.

Fig. 283.

The Kraemer and Sarnow method [1] is similar to the ball and ring method, except that the asphalt is contained in a 6–7 m.m. open glass tube, and 5 grams of mercury placed on the top, the tube being suspended in water near the bulb of a thermometer. The water is heated until the mercury drops through with the asphalt.

A recent electrical method [2] has been devised by Mr. Herbert Abraham, in which the temperature is raised by a coil of resistance wire placed in the bath. The coil is connected with a rheostat, by means of which the temperature can be easily regulated. The particular advantage of this method is the uniform rate at which the asphalt can be heated.

Penetration: (Consistency or hardness.). The instruments generally used are the Bowen, the Dow, and the New Yorking Testing Laboratory Penetrometers, all of which are described by Mr. Clifford Richardson in the "Modern Asphalt Pavement." A sample of the asphalt is subjected

[1] Chem. Ind. 1903, 26, (3), 55–57.

[2] Described by Mr. Herbert Abraham in Proceedings of American Society for Testing Materials, Vol. IX, 1909.

to the impression of a weighted standard needle for a specified time, at a definite temperature, the penetration of the needle being recorded on a dial.

Mr. Herbert Abraham, in the Proceedings of the American Society for Testing Materials, Vol. IX, 1909, describes his consistometer, which is said to give a more accurate measurement of the true hardness of asphalt than the penetrometers.

Petrolene and Asphaltene. The bitumen soluble in petroleum spirit has been designated arbitrarily "petrolene," and the part soluble in carbon-disulphide as "asphaltene." Some users of asphalt vary their specifications for petrolene and asphaltene, basing their proportions on what in practical work seems to give the best results. The petrolene is first determined by extracting a sample with petroleum spirit, the amount dissolved representing the petrolene; the residue is then extracted with carbon-disulphide, the part dissolved representing the asphaltene.

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XXIV

THE DESTRUCTIVE DISTILLATION OF WOOD

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The Distillation of Wood. Wood is a material that is found widely distributed. In some sections the various woods are equally intermingled, while in other sections large areas are covered by only one species, with but few trees of other kinds. In the United States there is a yellow pine belt reaching from North Carolina to Texas, the northern limit being Central Alabama, and extending south to within a few miles of the coast. The fir belt is found on the Pacific Slope and extends from northern California into British Columbia. In Michigan are found large tracts of maple, and in other States other kinds of wood are found in quantity.

For distillation purposes, usually but two classes of woods are used—the hard woods, such as oak and maple, and resinous woods, such as the yellow pine and Douglas fir. The hard woods yield larger quantities of acetic acid and alcohol and the resinous woods more tar and oils. To obtain the highest yields of the various products sought, the proper kind of wood must be selected, and the supply should be large.

Treatment of the Material Preparatory to Distillation. In hard wood distillation in the United States, the wood is cut into lengths of about 4 ft., like ordinary cord wood. In Europe the wood is often cut into short billets and then distilled. As the distillation of hard wood is now carried on mostly in connection with iron furnaces, large pieces of wood must be used in order to make a suitable charcoal.

The practice with resinous woods is very variable. Some plants use cord wood, some billets, and some chips from a chipping machine called a "hog."

In all destructive distillation processes, the finer the wood is cut the more quickly the distillation proceeds. To distil very fine material special apparatus is needed on account of the tendency of the material to pack, thus preventing the heat from passing through. Usually, in a stationary retort the wood should not be cut in pieces less than a foot in length. As the cutting of the wood requires power, labor and apparatus, the advantages of rapid distillation are often offset by the expense of preparation. For the extraction of turpentine, the finer the particles of

wood, the larger the yield, the quicker the distillation and the better the quality of the oil produced. If the residue is to be used for paper making, the chips should be of a suitable size to make the proper fiber.

Manufacturing Processes. For the production of charcoal only, the simplest and crudest form of distillation is the common charcoal pit, Fig. 284. This method consists of stacking up a lot of wood in a circle of 30 to 50 ft. in diameter and covering it with earth. These pits are made in various shapes and sizes. Often the wood is cut into billets and placed on end to form a circular stack of several layers, the diameter of each upper layer being less than the one immediately below it, thus forming a mound or "meiler." A passageway is left to the middle of the pile so that a fire can quickly reach the center. The pile is covered with turf and sand, except near the bottom, where vents are left for the admission of air and also for the escape of the vapors. In this form of distillation part of the wood is carbonized by the heat formed by the combustion of the other part. The water vapor is driven off first and the oxygen of the air present in the interstices of the wood is consumed. After distillation gets under way the air is carefully excluded to such an extent that only sufficient is admitted to thoroughly char the wood without burning too much of it. Any part exposed by the earth falling in is quickly covered and only cracks enough allowed to permit the gases to escape. The charring is finished when the gases become light blue in color. The earth is then removed in small sections at a time and the charcoal quenched with water.

Fig. 284.—Charcoal pit.

In a charcoal kiln the wood is stacked either on end or lying down. A firing passage is left as in the case of the charcoal pit. The kiln itself consists of a brick chamber, either beehive in shape or rectangular. They are usually made large enough to hold from 60 to 80 cords of wood. Some are lined with firebrick part way up the side Doors are left in the top and bottom for charging the wood. Openings are left in the bottom for the admission of air, and some have a flue connection with a stack so as to encourage the draft. Those having stacks can be forced so as to complete the distillation in two or three days if necessary. Usually it takes about eleven days to charge, distil and to cool.

An illustration of the most common form of kiln is shown with stack in Fig. 285. The method of operating a kiln is similar to that followed with

a pit. The fire is led to the middle of the pile and the whole allowed to heat slowly to drive out the water, then the holes at the bottom are closed and opened in such a manner as to cause the fire to spread over the entire kiln so as to avoid, as far as possible, the formation of brands or uncharred pieces. As with the pit, the presence of the light-blue vapors denotes the fact that most of the volatile matter has been driven off. The kiln is then closed up tightly with lime and allowed to cool. In both the pit and the kiln the vapors are lost, although sometimes a condenser is used with a kiln. On account of the large amount of fire gases which mingle with the vapors, these condensers must be large and supplied with plenty of cooling water. The yield of valuable products is much less than when retorts are used.

To manufacture tar from resinous woods by means of kilns or pits, it is customary to have a trough leading from the bottom of the wood to a pit underground. The wood is cut up much finer, and is more thoroughly burnt, leaving but little charcoal, the object being to obtain as much tar as possible.

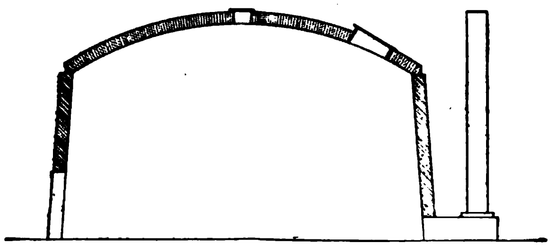

FIG. 285.—Charcoal kiln with stack.

Retorts. To save the volatile matter coming from the wood, various retorts have been devised, varying within wide limits, according to the kind of wood to be distilled. As already stated, with kilns and pits the volatile matter is lost or partially destroyed, owing to the admission of air directly to the wood.

The simplest form of apparatus for saving the vapors formed by distillation consists of an inclosed vessel, called a retort, surrounded by a suitable furnace, to which heat can be applied by means of coal, wood, oil, gas or electricity, the vessel to be supplied with a vapor pipe connecting with some form of a condenser. Some kind of tank is also needed in which to collect the condensed products. Where there is acid, the retorts are made of iron, the connecting pipes and condenser tubes of copper, and the receiving tanks of wood or copper lined. To distil steam for turpentine, a furnace would not be required, but the other apparatus would be similar.

Hard-wood Distillation. Using hard wood, destructive distillation is practised, the products sought being charcoal acetates and wood alcohol.

The retorts used are of two distinct types, those placed horizontally in the furnace and those set vertically. Of the horizontal type there

are two classes, the rectangular ovens and the cylindrical retorts. Of the vertical type there are three classes, the fixed retort, the removable retort and the fixed retort with removable cage.

Most of the retorts are made of boiler plate of a thickness of $\frac{3}{8}$ in. or more. Formerly cast-iron and clay retorts were used, but, although they do not burn out as readily as wrought iron, they must be made thicker to have the same strength, and have the further disadvantage of cracking when heated.

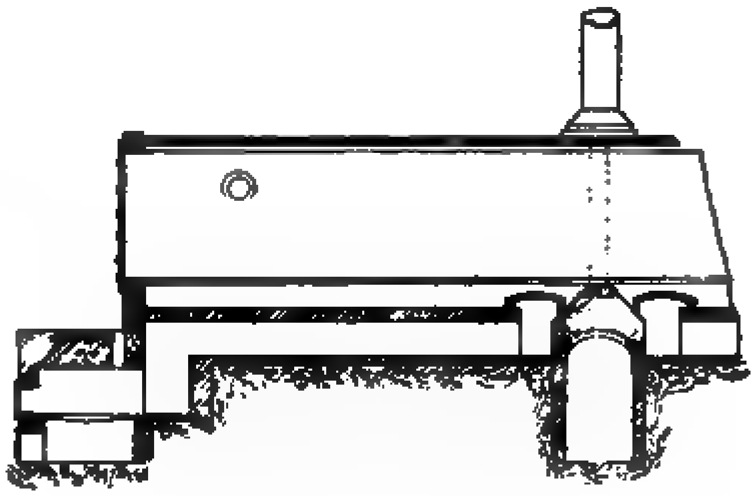

FIG. 286.—Steel oven.

Of the horizontal retorts the ovens are the most numerous — Fig. 286. They are rectangular in shape, flat on the bottom and slightly arched on top. The bottom is supplied with rails. On the sides or back are one or more openings for the exit of the vapors to be condensed. The wood is loaded on steel cars holding about two and one-half cords each and rolled into the retort. The ovens are about 6 ft. wide and 7 ft. high and of various lengths to hold two, three or four cars each. One or two coolers are used with each of these retorts, of similar shape to the retorts but of lighter material, into which the car of charcoal is withdrawn soon after the end of the distillation.

FIG. 287.—Cylindrical retort and condenser.

Some of the cylindrical retorts, Fig. 287, are made 9 ft. long by 50 ins. in diameter and will hold about a cord each. These retorts are charged and emptied by hand. An iron box mounted on wheels is used to hold the hot charcoal, and when full it is covered with a sheet-iron cover and the edges luted with sand or clay.

Of the vertical retorts no particular type seems to have the preference. The retorts are usually made cylindrical and hold from $\frac{1}{2}$ to 5 cords of wood. A convenient size is about 2 cords. The *fixed retorts* remain in the brickwork and are attached to the vapor pipe of the condenser by one or two pipes, preferably one at the top and one at the bottom. The *movable retorts* are so arranged that they can be pulled out of the furnace when the wood is charred and allowed to cool unopened. Instead of hoisting the retort itself some types use a retort with removable cage, Fig 287. Only the cage is removed, and as the cage does not have to stand the

direct heat of the fire, it can be made of lighter material than the retort, and the removing of the cage instead of the retort saves the wear and tear of the brickwork. In addition to this the vapor pipes are not disturbed.

The larger sizes of vertical retorts require suitable hoisting apparatus in order to charge the wood, and there is always danger of a rope breaking, thus causing much damage. The vertical retorts are much easier to charge and are easier to clean out than the horizontal ones, particularly while hot.

Condensers. The condensers used are generally of one type, although other kinds might be used. The most satisfactory seems to be the vertical tubular condenser which is shown in Fig. 288. It consists of a vapor pipe, leading to an expanding chamber at the top of the condenser; the necessary condensing tubes, and a bottom chamber for collecting the condensed matter from the tubes—these parts all made of copper. The whole is contained in an iron or wooden shell which holds the condensing water. The top of the condenser is supplied with a cap or removable top fastened by means of a yoke or bolts so that the tubes can be easily reached and cleaned. To the lower chamber is connected an outlet pipe which is usually supplied with a "goose neck" or U bend, to hold back the gases, and a top opening to permit the gases to escape to the furnace. The bottom of the condenser is made sloping so as to drain out the tar. Sometimes a few fractionating elements are used to remove the tar from the vapors, so as to make the pyroligneous acid free from tar, thus saving one distillation when making gray acetate of lime.

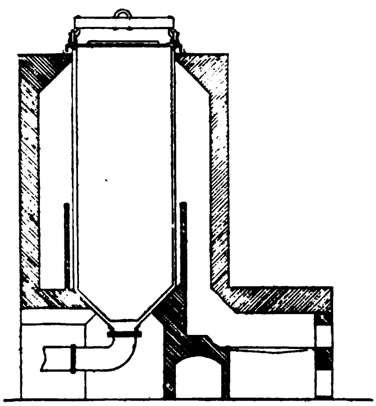

FIG. 288.—Vertical retort with removable cage.

Worm condensers have been used, and also tubes set one above the other, with removable ends, but they are not as satisfactory as the tubular condenser.

To carry out the *operation* of *destructive distillation* no definite rule can be followed. The temperature required varies with the different woods, and the time of distillation varies with the temperature. Some woods distil easily and others with difficulty. The yield of condensed products varies greatly with the method of firing. The charcoal made at a given temperature also varies in composition, according to the kind of wood used. The proper conditions should always be determined by experiment when a new variety of wood is used.

To operate to the best advantage it is best to heat slowly after the liquid starts to flow from the mouth of the condenser, as overheating

causes a loss of volatile matter. After reaching a certain temperature, the heating can be increased quite rapidly in order to drive out the heavy tars. The first distillate begins to come over at about 320° F. and consists of furfural, water and very little acid. The watery distillate is known as "pyroligneous acid." The percentage of acid increases with the temperature until the tar begins to distil, then it begins to drop off slightly. Meanwhile uncondensable gases are formed and these are piped to the furnace and burned. During the early stages of the distillation the color of the flame of the burning gases is blue, due to the carbon monoxide present, while later the color becomes yellow, due to the presence of the heavier hydrocarbons. The end of the operation is indicated by the falling off of the quantity of the distillate at the mouth of the condenser, by the temperature inside the retorts (about 800° F.), and by the color of the shell of the retort. The character of the distillate also indicates the end of the distillation, the tarry products being strongly in evidence. When cars or cages are used the charcoal is withdrawn hot, thus saving the heat of the brickwork for the next charge. The conditions should be regulated so that each retort can be charged once every twenty-four hours.

The Distillation of Resinous Wood. The distillation of resinous woods requires retorts varying in size and shape with the methods of operation and the products sought. The chief commercial products obtained by the distillation of resinous woods are turpentine, tar and charcoal. Soft woods yield a much larger amount of water than hard wood and this causes the pyroligneous acid to be weak in acetic acid and alcohol. On this account the pyroligneous acid from resinous woods is not usually saved.

There are several methods of treating resinous woods to obtain the various products. The apparatus in the various cases varies somewhat. The methods are as follows: 1. Destructive distillation, with or without steam. 2. Steam distillation. 3. Distillation of turpentine by means of hot rosin. 4. Extraction by means of hot water. 5. Extraction by means of volatile solvents.

The destructive distillation of resinous woods is carried on in a very similar manner to the treatment of hard wood. So far, both horizontal and vertical retorts have been used, varying in capacity from 1 to 5 cords. Various-shaped retorts have been used, and points of advantage claimed for each one. Generally the retorts are fitted with pipes and valves, so that the vapors can be drawn off different levels according to the relative gravity of the condensed products.

The greatest variation seems to be in the method of extracting the turpentine. As this substance is apt to become contaminated with tarry products, giving it a bad odor and color, considerable care is necessary to produce it. To avoid this contamination, some use two condensers, one for the turpentine and the other for the tar and pyroligneous acid. Others collect the turpentine in one tank and the other products in another.

Usually the change from turpentine to the other products is made when the temperature reaches 320° F., or when the wood begins to decompose.

The operation is carried on at first at a low temperature so as not to char the wood. The turpentine and resin exist already formed and are not products of the decomposition of the wood. By the influence of heat the turpentine distils, carrying with it part of the resin. Sometimes steam is added to help carry over the vapors. As the heat increases part of the resin decomposes and rosin oil distils over. When the wood begins to char, the pyroligneous acid begins to form and the distillation

AA. Retorts;
BB. Condensers;
CC. Pipe for condensed products;
DD. Receiving tank, crude liquors;
E. Oil tank;
FF. Acid and lime tee stills;
G. Neutralizing tank and filter press;
HH. Steam pans for acetate;
I. Finishing pan for acetate;
JJ. Rectifying still for alcohol;
K. Crude oil and tar still;
L. Washer for crude oil;
M. Column still to refine turpentine from crude wood oil.

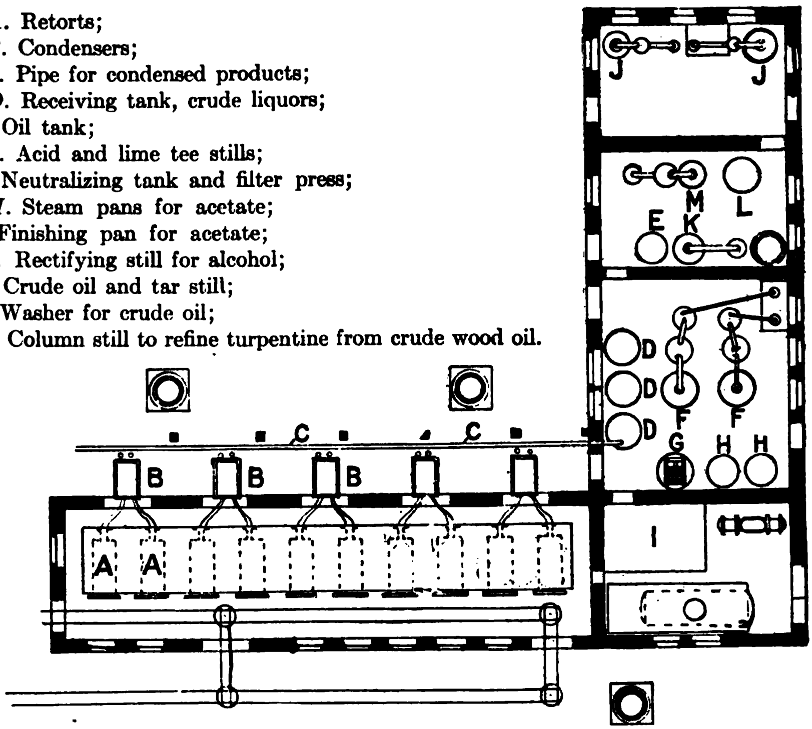

FIG. 289.—Plan of complete plant for distillation of resinous woods.

is carried on from this stage exactly as in the case with hard-wood distillation and the products all collected in one tank. See Fig. 289 for complete details of plant for destructive distillation of wood.

The Steam Process. To extract the turpentine, which is already present in the wood, it is only necessary to employ such agents as will volatilize it. A mixture of turpentine and water boils at 95° C., so if steam be passed through chipped wood in a suitable retort and the temperature maintained above 95° C., a mixture of oil and water vapor will distil and can be condensed in the ordinary manner. This is an old method of distilling finely divided wood that has been given much attention recently.

Much ingenuity has been used to devise suitable mechanical arrangements for carrying on the process successfully. The requirements are a wood chipping and elevating system that will deliver the wood to the retorts; an easy method of discharge from the retorts, for the steamed wood; and the proper conveying machinery to remove the discharge chips to a bin or to the boilers. Considerable steam is needed for this process.

Usually, a vertically placed or slanting retort (see Fig. 290) is used with an opening on top for the entrance of the wood, and with a large discharging device at the bottom. Various forms of rotating retorts are also used. The retorts are connected to suitable condensers.

The resinous wood is hogged, then elevated by means of a conveyor to the retorts or to a bin above the retorts. The retort is filled nearly full with wood and the opening at the top closed. Steam is allowed to enter and when the retort becomes warm enough the steam and oil vapors are led off to the condenser. A pressure of from 5 to 20 lbs. is generally maintained, so as to force the steam into contact with all parts of the wood. As the temperature is not high enough to affect the wood fiber, this process presents one of the best methods for obtaining a clear white oil from the wood in a short time. If enough steam be used all the turpentine can be extracted in less than one hour. The commercial importance of the process seems doubtful, as the yield is not sufficient to pay for the increased cost necessary to obtain selected wood. Where a market can be obtained for the chips the process can be operated to advantage. However, the resin is lost and a process is desirable where the resin can be extracted with the turpentine.

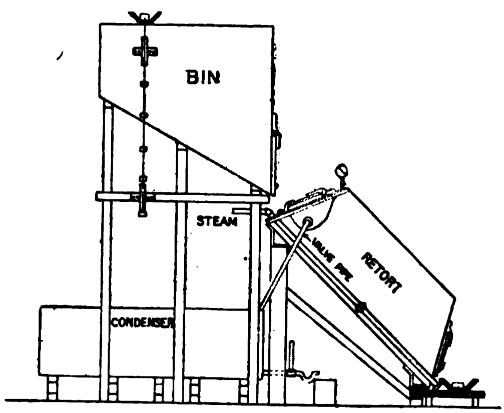

FIG. 290.—Slanting retort for turpentine.

During the digesting process, while making paper from yellow pine by the soda process, the turpentine from the blow-off at the top is condensed and recovered very economically. The product is not as good as when made by the steam process direct, the pressure being too high.

Resin Process. To avoid the local overheating during the early stages of the destructive distillation process, which causes part of the wood to distil before the temperature of the whole reaches 320° F., some have attempted to distil the wood in a bath of rosin. The process is said to work well, but it is doubtful if continued operation confirms first impressions. The distilling point of the resin is too close to that of wood, the

rosin itself is liable to be decomposed by local overheating, and being solid at ordinary temperatures, difficulty would be experienced in pumping it and removing it from the wood at the end of the operation. It will probably have no future.

Hot-water Process. A more rational process would be the hot-water process, provided the temperature could be raised to the proper degree. Although turpentine and water begin to distil at 95° C., a mixture of turpentine and resin in wood requires a higher temperature to extract the turpentine and to liquefy the resin. This process on a small scale is said to give large yields of both turpentine and rosin from the right kind of wood.

Extraction Processes. Extraction processes seem to be the most rational way of treating very resinous wood, particularly if charcoal is not to be made. Two products are thus obtained and the cost of operation need not be much greater. The success of such processes naturally depends upon the substance used in extracting and the cost of treatment necessary to recover it. Several substances have been suggested and tried.

The *Craighill and Kerr* process requires the use of dilute caustic soda to hold back the resin and acids, before steaming, to distil the turpentine. After the turpentine has been removed, the wood is submerged with water, steam applied and the wood digested at a temperature equal to the boiling-point of the alkaline solution with which the mass was saturated, and the digestion continued until the rosin has completely entered into combination by saponification with the alkaline solution. Thereupon the solution is drawn off and the wood well drained. The rosin is recovered by adding acid to the solution to neutralize the soda. The fiber is then to be made into paper. The *Frankforter* process requires the use of ether, carbon bisulphide, carbon tetrachloride, gasoline, etc.

The *Harper* process consists in the treatment of the chipped wood with turpentine, either hot or cold, the turpentine being made from the wood at the plant. The resin dissolves in the turpentine and the mixture is siphoned off. The wood is then steamed and the adhering turpentine removed exactly as in the steam process. The mixture of turpentine is heated in a suitable still with or without live steam, the turpentine distilling and the resin remaining behind in the still. In this way there is no cost for solvent, and the solvent is recovered and continually reused. The exhausted fiber is burned under the boilers, but could be used for making paper, or for making charcoal by distillation in a special retort. There is great loss of solvent in the use of these processes.

To Obtain Refined Products. The condensed liquor from the destructive distillation processes consists of three layers, the upper layer of tarry oils, the intermediate layer of pyroligneous acid, and the bottom layer of tar. Sometimes with resinous woods the line of demarcation is not very well defined. In such cases the separation is difficult, without distilling. A centrifugal separator could be used to advantage.

The crude product coming from the wood in the steam process consists of crude turpentine as an upper layer and of water as a lower layer. In all the processes the separation is effected as far as possible by gravity, the different products being drawn off at the respective levels, or one drawn off after the other.

Acetic Acid. The pyroligneous acid contains fatty acids, chiefly acetic, varying from 4 to 10 per cent, about 1 to 12 gals. of wood alcohol to the cord of wood used, some acetone, light oil, metacetone and other ketones, aldehydes and tarry products. To obtain the various products different means are pursued according to the quality of products to be made. These are brown acetate of lime or lead, gray acetate of lime, acetate of soda, acetic acid and refined wood alcohol.

To make brown acetate of lime, the acid is simply neutralized with lime and the insoluble tarry products produced skimmed off. The solution of acetate is distilled in an iron or copper still until the wood alcohol is collected, then the remaining liquor is evaporated to dryness and partially charred to destroy tarry matters.

To make gray acetate of lime, the liquor is sent to an acid still, a copper still with or without special fractionating column. The alcohol distils first and may be collected separately until the temperature in the still approaches 100° C. or the sp.gr. of the distillate is 1. The acid is then distilled and may be passed directly as a vapor through milk of lime, or condensed and caught separately, when it is known as distilled wood vinegar. This is neutralized with lime. As some of the acid may distil with the wood alcohol, both are sometimes condensed together and neutralized with lime. The liquor is then distilled in a fractionating still to recover the alcohol. The acetate liquor is then evaporated to dryness in suitable pans. Crude hydrochloric acid is often added before evaporation and the liquor drained from the deposit formed. The pans are usually provided with a set of stirrers to prevent the acetate from burning to the bottom. The tarry matter rising to the surface is removed through a sliding door. When the specific gravity (measured hot) reaches 1.116 the separation of acetate begins and gradually the mass forms a thick paste which is removed and spread on flat iron pans to be dried. Some finish the drying in rooms heated by the waste furnace or retort gases. The residue in the stills is " boiled tar," and is removed at intervals as it accumulates.

Acetate of soda is made in a similar manner to acetate of lime. Sodium carbonate is added, in small portions at a time to avoid too much effervescing, to distilled wood vinegar until the acid is neutralized. The tarry substances appearing on the surface are removed and the brown fluid, after clarifying by standing, is drawn off into shallow iron pans which are heated by the fire gases from the retorts or by steam. The liquid is boiled down to 1.23 sp.gr. then crystallized in sheet-iron boxes. The crystals are drained from the mother lye and then centrifuged. By calcining these

crystals, redissolving and recrystallizing a very pure salt is obtained. Sometimes the solution is filtered through bone-black or boiled with 10 per cent of bone-black and after recrystallizing and centrifuging an entirely pure salt is obtained.

Wood Alcohol. The crude wood alcohol is treated with lime and settled, the clear liquor being redistilled in column stills until of about 82 per cent by volume. By again redistilling, a product of 92 to 95 per cent can be easily obtained. However, to make alcohol that is miscible with water, it is advisable to dilute the alcohol with water until the specific gravity reaches 0.934 and allow the mixture to rest for a few days, when the greater portion of the hydrocarbons separate as an oily layer on the top and can be drawn off. The alcoholic fluid left is redistilled over lime and makes strong alcohol that does not become turbid upon the addition of water. The oily fractions are mixed together and redistilled separately, when a further quantity of alcohol is obtained. Only the portion miscible with water is saved, the other portions being worked over. The first runnings of the distillate are more or less colored, but the middle fractions are colorless and yield good alcohol. After the middle portion distils the alcohol begins to contain oil and it becomes non-miscible. Subsequently, the distillate becomes turbid and finally a mixture of oil and water comes over, which separates into two layers.

Acetone. None of these processes serve to remove acetone. To do this several methods are used. One is to form a compound of wood alcohol and calcium chloride, which is stable at 100° C. By gently heating, the acetone is driven off, and then by adding water and raising the temperature to 100° C. the calcium chloride compound decomposes and the methyl alcohol distils. Another method is to add caustic potash and iodine until the yellow color disappears, then to distil. The watery alcohol is repeatedly rectified over lime, and finally over metallic sodium or phosphoric anhydride to remove the last traces of water.

The Crude Tar. The tar from hard woods that is to be utilized is washed with water or dilute milk of lime, in order to wash out the acid that was not thoroughly separated by settling. It is then ready for further treatment. The tar from resinous woods is distilled with live steam in a copper tar still until the oils are removed. If these oils contain turpentine as they would when the distillate is collected together, they are specially refined. When thick enough the tar is ready for barrelling.

Tar Oils. To obtain tar oils from the tar, it is destructively distilled in a wrought or cast-iron vessel sometimes provided with a stirrer. The general shape of the still is similar to a turpentine still. Fig. 291. The still is heated slowly and the distillate collected until the specific gravity of the tar oil reaches about 0.98 when the receiver is changed. Following the light oils, a heavy oil comes over, having a specific gravity of upwards of 1.01 and of a yellowish green color. The distillation is sometimes carried on until nothing but coke is left in the still but it is usually better

to stop with the production of pitch which can be drawn out hot from the still. This is run out on iron plates to cool, care being taken to prevent ignition. The condensate is sometimes divided according to the temperature of distillation, the light oils being collected up to 240° C. and the heavy oils between 240 and 290° C. The heavy oil contains most of the creosote, which is extracted from the heavy oil by means of caustic lye of about 1.2 sp.gr. The hydrocarbons are boiled out and the creosote separated by neutralizing with sulphuric acid. The treatment is repeated and the final creosote distilled, the product coming over between 200 and 220° C. being called commercial wood creosote. To further purify it, it is oxidized with a mixture of dichromate of potassium and sulphuric acid and again distilled. The crude oil in the distillate from the steam treatment of pine tar is often saved. It varies in color from light yellow to brown, exposure to the air causing the color to become much darker. A number of substances are present, the oils coming from the distillation of the turpentine and from the destructive distillation of the resin in the wood. The crude oil contains considerable quantities of creosote and tar products. To remove these, the oil is redistilled in a still of similar shape and construction as the tar still—only smaller. Fig. 291. The oil comes over with only a slight coloration. To prevent this color, the crude oil is sometimes treated with chemicals such as caustic soda, lime, permanganate, sulphuric acid and the like before being distilled. These substances usually fail to remove either odor or color to any great extent. When the percentage of turpentine in the wood oil is large, the crude oil is washed with water or alkali in an agitator and often distilled in a column still similar to the still used in refining wood alcohol.

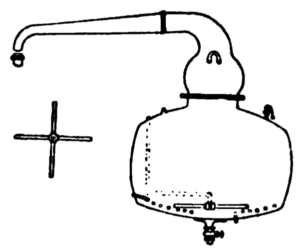

Fig. 291.—Turpentine and tar still.

Turpentine. The crude wood turpentine caught separately when wood is distilled by any method, is usually refined in order to make a marketable article. When the oil is very impure a still with a short column is desirable. When the oil is relatively pure and almost colorless like that obtained in the steam distillation, a simple distillation is all that is needed. Fig. 291. The oil should be tested as it comes from the still and when the specific gravity reaches 0.875 the receiver should be changed or the distillation ended. A heavy oil remains behind, which can be distilled at a higher temperature. This oil should not be mixed with the turpentine, as the mixture does not dry readily.

Sometimes the turpentine is treated like crude oil, with caustic soda, sulphuric acid and permanganate, but such treatment is not desirable if it can be avoided. As shown in Fig. 289, the crude oil is sometimes washed in a vessel fitted with stirrers.

Acetic Acid. This acid is not usually prepared directly from wood vinegar although it can be with considerable trouble. It is usually prepared by the decomposition of some acetates. Some of the acetates are decomposable by heat into acetic acid and oxides, for example lead acetate. The diacetates of sodium and potassium yield a very concentrated solution of acid when heated.

Usually, it is best to start with acetate of lime or soda and to distil with concentrated hydrochloric acid in a copper still, care being taken to have an excess of the salt in the still. When brown acetate of lime is used, it is previously roasted at a low temperature. The acid formed is colored and contains about 50 per cent of anhydrous acid. With dilute acid in the still, the acid is purer, but contains only 30 per cent anhydrous acid. Often the acid is distilled in Marx vessels and filtered in towers through freshly burned charcoal. To obtain stronger acid, the weak liquor is redistilled and the stronger parts of the distillate caught separately. Any HCl that may be found in the distillate can be removed by rectifying over acetate of lime or soda. Sulphuric acid could be used to effect the distillation, but the operation is not so smooth and the distillate is apt to contain sulphur dioxide.

Glacial acetic acid can be prepared by distilling 12 parts by weight of pure anhydrous sodium acetate with 11 parts of concentrated sulphuric acid. The first portion of the distillate is rectified over sulphuric acid and pyrolusite to remove traces of sulphurous acid. The last portion, which is frequently empyreumatic, is collected by itself. The water in the 50 per cent acid can be removed by distilling with anhydrous calcium chloride and cooling the distillate, whereby one portion crystallizes. The liquid portion is drawn off and again distilled over calcium chloride. By distilling strong acid over fused and coarsely powdered potassium acetate and changing the receiver at 120° C. the glacial acetic acid will pass over in the last portion. This is again rectified over potassium acetate and the distillate cooled to about 16° C. to crystallize the acid. Stoneware vessels are needed to carry on the distillation as the acid strongly attacks metals. Sometimes copper stills are used with silver necks and worms. An attempt is also being made to use aluminum.

Acetone. On a commercial scale, acetone is made by the dry distillation of gray acetate of lime at 290 to 400° C. in retorts which are connected with a cooling apparatus. When brown acetate is used it is previously roasted at 230° C. The first runnings are weak in acetone but the percentage increases with the temperature. The distillate separates into two layers, the " heavy acetone oils " on top and the lighter oils dissolved in water on the bottom. The yield is about 20 per cent of the calcium acetate. The crude acetone is treated with lime and distilled in column stills in a similar manner to wood alcohol, a nearly pure product being obtained.

The nearly pure acetone can be purified by treatment with sodium bisulphite and crystallizing the compound formed.

Chemical Theory and Reactions Involved in the Distillation of Wood. Wood consists essentially of cellulose $(C_6H_{10}O_5)_n$ with sap and incrusting lignin. Green wood contains varying amounts of water up to about 50 per cent by weight. Air dried wood contains about 20 per cent of moisture which can be eliminated by heat, but is reabsorbed by exposure to the air. Various chemicals affect cellulose, but it is usually a very resistive substance. When burned, wood leaves an ash varying in amount with the kind of wood. Resinous woods contain in addition to the woody fiber, a large amount of resins and oils which can be extracted by solvents, leaving the fiber intact. The oil is chiefly terpene the principal ingredient of turpentine, and the resin is chiefly colophony.

Cellulose being a complex organic substance the chief influence of heat is naturally to decompose it into simpler compounds. From its composition, it would be expected that by driving off the water, 44.45 parts by weight of charcoal would be obtained. It breaks down, however, into more complex substances than water and carbon. A relatively high temperature is needed to start the decomposition and the temperature must be continually increased during most of the distillation in order to continue the decomposition.

Cellulose may be considered a hexahydric alcohol $C_{12}H_{14}O_4(OH)_6$. From the yield of charcoal the final products of distillation might be written

$$C_{12}H_{20}O_{10} = 8C + C_4H_{20}O_{10}$$
$$100 = 29.6 + 70.4.$$

The $C_4H_{20}O_{10}$ may be considered to have arranged itself in various ways in order to form the tar, acetic acid, methyl alcohol and gas. For examples of the possible changes the following are given.

1. $C_4H_{20}O_{10} = \underset{\text{acetic acid}}{2C_2H_4O_2} + \underset{\text{water}}{6H_2O}.$
2. $\underset{\text{acetic acid}}{C_2H_4O_2} = \underset{\text{wood alcohol}}{CH_4O} + \underset{\text{carbon monoxide}}{CO}.$
3. $\underset{\text{acetic acid}}{C_2H_4O_2} = \underset{\text{marsh gas}}{CH_4} + \underset{\text{carbon dioxide}}{CO_2}.$
4. $\underset{\text{acetic acid}}{2C_2H_4O_2} = \underset{\text{acetone}}{C_3H_6O} + \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{H_2O}.$
5. $\underset{\text{acetone}}{2(C_3H_6O)} = \underset{\text{metacetone}}{C_6H_{10}O} + H_2O.$
6. $\underset{\text{acetic acid}}{C_2H_4O_2} + CO = \underset{\text{aldehyde}}{C_2H_4O} + CO_2.$
7. $\underset{\text{methane}}{2CH_4} = \underset{\text{acetylene}}{C_2H_2} + H_6.$
8. $10CH_4 = \underset{\text{naphthalene}}{C_{10}H_8} + H_{32}.$

The products of distillation seem to be water, fatty acids, hydrocarbons, phenols, guaiacol, alcohols, aldehydes and ketones. The methyl group seems to predominate. The method of decomposition is difficult to

determine and at present the yields of the various substances are the only guide. These vary much when the wood is heated rapidly and the influence of local heating is a disturbing factor. An increase of temperature inside of the retort over that in the furnace indicates that at one stage of the distillation at least heat is evolved by the decomposition of the material inside of the retort. The analysis of the wood partly charred leads to the conclusion that while some of the acetic acid is coming off the decomposition takes place according to the following equation:

$$(C_6H_{10}O_5)_2 = \underset{\text{partly charred wood}}{2C_4H_6O_3} + \underset{\text{loss}}{2C_2H_4O_2}.$$

The gas formed at the same time comes from the acetic acid as in 2, 3, 4, 6 and 7, and the excess water from the moisture still present in the wood.

The refined products are made in accordance with better known theories. The acetates are made according to the well-known formula.

$$\underset{\text{base}}{ROH} + \underset{\text{acetic acid}}{CH_3COOH} = \underset{\text{acetate}}{CH_3COOR} + \underset{\text{water}}{H_2O}.$$

The wood alcohol is refined when distilled, according to the theory pertaining to miscible liquids, which in the case of alcohol and water would be that the boiling point is higher than the temperature at which the sum of the maximum or saturation tensions of the two separate vapors is equal to the external pressure and that at any given stage of the distillation, the alcohol is more abundant in the vapor than in the mixed liquids in the still. Thus the percentage of alcohol increases with repeated distillations.

The turpentine distils with steam according to the law of immiscible liquids, which states that distillation will take place at the temperature at which the sum of their vapor pressures is greater than that of air. The quantity of each liquid found in the distillate is pr portional to the vapor density. With crude liquors, the temperature and proportions would be different because the impurities may or may not be immiscible with water and the system w uld be altered

The distillation of the other products such as wood oil from tar is similar to that of turpentine, but the system is comprised of three substances, tar and oil miscible with each other in nearly all proportions, and water which is not miscible with either the tar or the oil.

Acetone is formed by the destructive distillation of acetate of lime (or other acetate) according to the formula.

$$(CH_3 \cdot CO \cdot O)_2 \cdot Ca(CH_3 \cdot CO \cdot O)_2Ca = 2(CH_3 \cdot CO \cdot CH_3) + 2(CaO \cdot CO_2).$$

The destructive distillation of the tar presents more difficulties from a theoretical standpoint than that of wood. The substances constituting it are more varied and the reactions would be still more complex.

XXV

OILS, FATS AND WAXES

ALLEN ROGERS

Classification. In this chapter will be included those substances which consist primarily of the higher fatty acids in combination with glycerol, thus distinguishing them from the mineral oils described in Chapter XXIV. From their physical appearance it is not possible to give a definite classification for what would be considered a solid fat in a temperate climate might be a liquid in a warmer locality. Roughly, however, we may class certain ones as liquid fats or oils, and others as solid fats, or fats. There is, on the other hand, a distinct difference between fats (fatty oils and solid fats), and waxes; for the latter, as a rule, are formed by the union of fatty acids with alcohols not belonging to the glycerol series.

"The most convenient classification of fats (fatty oils and solid fats) for practical purposes, appears to be given by arranging them according to the magnitude of the iodine value. This principle leads, without unduly forcing it, to a natural subdivision into liquid fats and solid fats, the former being differentiated from the latter by the considerably higher iodine value. Hence, an arrangement based on the magnitude of the iodine value would include the older system of classification according to consistency. Inasmuch as the magnitude of the iodine value stands in close relationship to the absorption of oxygen, or, in other words, to the drying power, classification on the iodine value would also include the older subdivision into drying and non-drying oils." (Lewkowitsch.)

Arranged in this manner are the following subdivisions:

I. *Liquid Fats and Fatty Oils.*
- *A*. Vegetable oils
  1. Drying oils
  2. Semi-drying oils
  3. Non-drying oils
- *B*. Animal oils
  1. Marine animal oils
     - (*a*) Fish oils
     - (*b*) Liver oils
     - (*c*) Blubber oils
  2. Terrestrial animal oils

II. *Solid Fats.*
- *A*. Vegetable fats
- *B*. Animal fats
  1. Drying fats
  2. Non-drying fats

III. *Waxes.*

A. Liquid waxes

B. Solid waxes
1. Vegetable waxes
2. Animal waxes

Constitution of the Fats. The fats are combinations of glycerol with fatty acids. Glycerol being a tri-hydric alcohol will combine with one, two, or three acid radials, thus forming mono-glycerides, di-glycerides, and tri-glycerides. The last class, however, is the most important, as it is this condition which is supposed to exist in the neutral fats. The following graphic formulas will more clearly emphasize the three possible combinations:

$$
\begin{array}{llcl}
 & & \mathrm{H} & \\
 & & | & \\
\textit{Monostearin.} & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\
 & \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & & \mathrm{H} & \\
\end{array}
$$

$$
\begin{array}{llcl}
 & & \mathrm{H} & \\
 & & | & \\
\textit{Distearin.} & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & \mathrm{HO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & & \mathrm{H} & \\
\end{array}
$$

$$
\begin{array}{llcl}
 & & \mathrm{H} & \\
 & & | & \\
\textit{Tristearin.} & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & \mathrm{C_{17}H_{35}COO}— & \mathrm{C} & —\mathrm{H} \\
 & & | & \\
 & & \mathrm{H} & \\
\end{array}
$$

It will be seen that not only is it possible to have compounds in which one acid enters into the combination, but also others, known as mixed glycerides, in which two or even three different acid radicles may be joined to one glycerol group. This is thought by some to account for the fact that practically all of the common oils are mixtures, rather than simple esters. Our present knowledge, however, does not warrant any definite conclusion in this matter.

The fatty acids occurring in the more common oils, together with a few of their constants, will be found in the table on page 547.

SATURATED ACIDS: $C_nH_{2n+1}COOH$

Acid.	Formula.	C°	Sp. Gr.	Melting Point C°.	Ref. Index C°.
Butyric	C_3H_7COOH	20	0.959	-6.5	1.3990 at 20
Isovaleric	C_4H_9COOH	20	0.931	-51	....
Caproic	$C_5H_{11}COOH$	20	0.924	-8	1.4163 " 20
Caprylic	$C_7H_{15}COOH$	20	0.910	16.5	1.4282 " 20
Capric	$C_9H_{19}COOH$	40	0.8858	31.4	1.4285 " 40
Lauric	$C_{11}H_{23}COOH$	20	0.883	43.6	1.4266 " 40
Myristic	$C_{13}H_{27}COOH$	60	0.8584	53.8	1.4307 " 60
Palmetic	$C_{15}H_{31}COOH$	60	0.8527	62.6	1.4269 " 80
Stearic	$C_{17}H_{35}COOH$	80	0.8386	69.3	1.4300 " 80
Cerotic	$C_{25}H_{51}COOH$	79	0.8359	78	....
UNSATURATED ACIDS, $C_nH_{2n-1}COOH$					
Tiglic	C_4H_7COOH		0.9641	64.5	....
Oleic	$C_{17}H_{33}COOH$		0.898	14	1.4603
Erucic	$C_{21}H_{41}COOH$	.....	....	34	....
OTHER UNSATURATED ACIDS					
Linoleic	$C_{17}H_{31}COOH$	14	0.9206	....	....
Linolenic	$C_{17}H_{29}COOH$		0.9228	....	....
Ricinoleic	$C_{17}H_{32}OHCOOH$	15.5	0.9509	4	....

The fatty acids are all lighter in weight than water. Those having less than ten carbon atoms may be distilled, and are known as the volatile fatty acids. Those containing more than ten carbons cannot be distilled without decomposition and are known as non-volatile fatty acids. The oils containing the saturated acids do not undergo any change when exposed to the air. On the other hand those which contain the unsaturated acids become gummy, and in certain instances when exposed in thin layers form dry, hard films. This change is called drying, and is most marked in the case of those oils containing glycerides of linoleic, linolenic, and ricinoleic acids.

LIQUID FATS

Vegetable Oils. The usual method of obtaining the oils is by crushing that part of the plant richest in oil, and subsequently pressing the ground pulp thus obtained. Extraction with benzine or other solvent is also employed. The crushing may be secured by means of the edge-runner, Fig. 6, or by means of heavy steel rollers arranged in vertical series. The crushed material is then placed in canvas bags, and subjected to hydraulic pressure. The first pressing is usually done in the cold as a lighter color, and better quality is thus obtained. During the second pressing the pulp is heated thereby producing a larger yield, but of an inferior quality. By further heating a final oil is obtained known commercially as "foots." The extraction process consists in treating the ground pulp contained in closed vessels, with benzine, naphtha or other solvents. The extract is subjected to distillation in order to recover the solvent,

leaving the fats in the still. Although this method gives a larger yield than is possible by pressing, it is not generally employed on account of the risk from fire, the cost of installation, and impossibility of using the press cake as a cattle food.

Vegetable Drying Oils. Drying oils are characterized by their power to absorb oxygen from the air, thus forming an elastic film. The amount of this absorption is in proportion to the iodine value; so that we may easily judge of the drying quality of an oil from its iodine number.

TABLE OF CONTENTS FOR DRYING OILS

Name of Oil.	Yield from Seed Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Perilla..........	35.8	0.9306	20°C	189.6	206.1	....	....
Linseed.........	38–40	0.9315–45	15°C	192–195	171–201	1.4835	22°C
Tung...........	40–41	0.9360–432	15°C	193.	150–165	1.5030	19°C
Hemp..........	30–35	0.9255–80	15°C	192.5	148	1.4780	15.5°C
Poppy..........	41–50	0.9240–70	15°C	195.	133–143	1.4586	60°C
Sunflower.......	21–22	0.9240–58	15°C	193.5	119–135	1.4611	60°C
Tobacco seed....	38–40	0.9232	15°C	170.	118.6	....	....

Perilla Oil. This oil occurs to the extent of 35.8 per cent in the nuts of the *Perilla ocymordes*, a plant indigenous to East India, Manchuria, and Japan. It has the highest iodine value of any known oil, and in odor and taste resembles linseed oil. Its drying quality, however, is inferior to linseed oil, due to its peculiar property of forming drops when spread on a hard surface.

Linseed Oil. This oil has been discussed, with other drying oils in Chapter XVIII. It is obtained from the seeds of the flax plant, grown extensively in Russia, India, Argentina, Canada and the United States. On cold pressing, a light yellow oil is obtained used to a limited extent as an edible oil. By far the greatest quantity, however, is used in the manufacture of paint and varnish. The chemical composition of linseed oil is not well known, although indications point to about 10 per cent of glycerides of solid fatty acids, equal parts palmetic and myristic acids. The liquid glycerides consist of 5 per cent of oleic acid, 15 per cent of linoleic acid, 15 per cent of linolenic acid, and 65 per cent of isolinolenic acid.

Tung Oil. This oil is sometimes spoken of as "Chinese Wood Oil." It is obtained from the seeds of *Aleuriter cordata,* a tree indigenous to China and Japan. The oil varies to some extent according to its source. The seeds are usually roasted, broken into a powder and pressed. The cold pressed oil is pale yellow, and is known in the trade as " white tung oil." That resulting from hot pressing is dark in color, and termed " black tung oil." Its principle use is in paint and varnish manufacture. Its chemical constitution differs from linseed in that it consists almost wholly of glycerides of oleic and elaeomargaric acids.

Hemp Seed Oil. The source of this oil is the hemp plant, *Cannabis sativa.* The color of the fresh oil is light green, becoming brownish yellow on standing. The solid glycerides of hemp oil are claimed to be those of stearic and palmitic acids. The liquid glycerides contain linoleic, oleic, linolenic, and isolinolenic acids. It is used as a paint oil, for making soft soaps, and low grades are employed for certain varnishes.

Poppy Oil. To obtain this oil the seeds are pressed cold, thus producing a product almost colorless, or very pale golden yellow, known in the trade as "white poppy seed oil." That expressed at a higher temperature is known as "red poppy seed oil." It is cultivated largely in Asia Minor, Persia, India, Egypt, and Russia. It is used largely as a salad oil, and in the manufacture of artists colors.

Sunflower Oil. This oil is obtained from the seeds of the *Helianthus annuus.* It is of a mild taste, pleasant odor, and a pale yellow color. It is raised extensively in Russia, Hungary, India, and China. It is employed in soap making, and for the manufacture of varnish. This oil does not dry as readily as those previously mentioned.

Tobacco Seed Oil. The oil obtained from the seed of the tobacco plant is of a pale greenish yellow color, and dries very readily. On account of its high price it has never found any commercial application.

Vegetable Semi-drying Oils. These oils form a connecting link between the drying oils and the non-drying oils, although it is difficult to say to which class they belong. Chemically they differ from the drying oils by the absence of linolenic acids; and from the non-drying oils by the linoleic acid they contain.

TABLE OF CONSTANTS FOR SEMI-DRYING OILS

Name of Oil.	Yield from Seed, Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Soja bean.....	18	0.9242–70	15°C	192.7	121.7	1.4762	15.5°C
Pumpkin seed..	35–37	0.9237	15°C	188.4	123–130	1.4723–38	25°C
Corn..........	6–10	0.9213–55	15.5°C	188–193	113–125	1.4750–70	15.5°C
Cotton seed...	24.26	0.9220	15°C	193–195	108–110	1.4743–52	15°C
Sesame.......	50–57	0.9230–37	15°C	189–193	103–108	1.4748–62	15°C
Croton.......	53–56	0.9500	15°C	210–225	102–104	1.4768	27°C
Rape.........	33–43	0.9132–68	15.5°C	170–179	94–102	1.4720–57	15°C
Castor........	46–53	0.9600–79	15.5°C	183–186	83–86	1.4799	15°C

Soja Bean Oil. This oil is also known as soy bean oil. It is obtained from the seeds of several varieties of the *Soja hispida,* a plant growing in China, Manchuria and Japan. The oil is mostly employed for edible purposes, although recently its use as a paint and soap oil is being considered.

Pumpkin Seed Oil. In South Russia the seeds of the *Cucurbito pepo* are roasted, and the oil expressed in the hot condition. This produces a viscous product of a deep red color. The cold pressed oil has a greenish

color and a slight red fluorescence. The cold pressed oil is used for edible purposes, while the inferior grades serve as burning oils.

Corn Oil. This oil is obtained from the germ of the maize plant, *Zea mays,* during the manufacture of corn starch. The freshly prepared oil has a pale yellow color, and may be readily identified by its taste which is similar to that of corn meal. It is coming into quite extensive use in the manufacture of soap and to a more limited degree in the manufacture of paint.

Cotton Seed Oil. This oil is obtained from the seed of the cotton plant, extensively cultivated in the United States, Egypt, East India, and other countries. The oil as it comes from the hydraulic press is dark or almost black. To remove this color the oil is treated with a small amount of dilute caustic soda solution which combines with the coloring matter and free fatty acids. On standing the soap formed settles out, leaving a slightly yellow supernatant oil. This oil is then drawn off and washed with warm water. For commercial purposes the darker product is usually bleached with chloride of lime and mineral acid, then thoroughly washed.

The market brands "summer oil" and "winter oil" differ from each other in that the latter has most of the stearine removed; so that the oil does not solidify during the colder months. Winter oil is sometimes spoken of as "demargarinated." The "cotton seed stearine" is of a light yellow color of the consistency of butter. It is manufactured on a very extensive scale in this country by cooling the oil, filtering off the solid deposit and pressing.

Cotton seed oil is used in large quantities for edible purposes, but owing to popular prejudice it seldom appears under its true name. We may find it on the open market as "table oil," "salad oil," "sweet nut oil" as well as a score of other designations. Large quantities of the cotton seed stearine are employed in the manufacture of "oleomargarine," butter compounds, butter substitutes, lard compounds, and lard substitutes. Cotton seed oil being cheap is often used as an adulterant for the more expensive oils, such as olive, peanut and other edible oils. Its chief use, however, is in the manufacture of toilet and laundry soaps.

Sesame Oil. This oil is obtained from *Sesamum orientale,* extensively grown in India, China, Japan, the Levant, and West Africa. The cold pressed oil is of a light yellow color, with a pleasant taste, so that it is used to some extent for edible purposes. The hot pressed oil is used largely in soap making.

Croton Oil. Croton oil is obtained from the seeds of *Croton tiglum,* a tree grown on the Malabou Coast, in Southern Asia, and in China. The oil varies in color from yellow, orange, or brown according to age. It has a nauseating odor, a burning taste, and a very powerful purgative action. Its chief use is in pharmaceutical preparations.

Rape Oil. There are several varieties of this oil, depending upon the place of cultivation. The oil is obtained from the seeds of *Brassica campestris.*

Castor Oil. This oil is obtained from the seeds of *Ricinus communis*, a plant grown extensively in East India, Java, the Mediterranean countries, and the United States. The cold pressed oil is used for medicinal purposes. The lower grades are used very extensively in manufacturing operations, such as leather dressings, and in the sulphonated condition is known as "soluble oil" or "Turkey red oil." Castor oil is a colorless or pale greenish oil with a mild taste.

Vegetable Non-drying Oils. The oils in this class have a lower iodine number than those of the two preceding classes. They do not become gummy when exposed to the air at ordinary temperature; although they all thicken on heating.

Name of Oil.	Yield from Seed, Per Cent.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Peach kernel.....	32.35	0.918 0.9215	15°C	191.5	93.3– 100.3	1.4713	15°C
Almond.........	45–55	0.9175 0.9195	15°C	199.3	100.7	1.4731	15.5°C
Peanut.........	43.45	0.9170– 0.9209	15°C	191.3	94.7	1.4766	15.5°C
Olive...........	40–60	0.916–18	15°C	185–196	79–88	1.4698– 1.4716	15°C
Olive kernel......	12–15	0.9184– 0.9191	15°C	183	87.4	1.4682	25°C

Peach Kernel Oil. This oil is obtained from the kernel of the peach, is of a pale yellow color, and greatly resembles almond oil. Its chief use is as an adulterant for almond oil.

Almond Oil. Almond oil is expressed from bitter almonds, which yield more oil than sweet almonds, although both oils are practically identical The source of this oil is Morocco, Canary Islands, Portugal, Spain, France, Italy, Sicily, Syria, and Persia. Its chief use is in pharmaceutical preparations.

Peanut Oil. This product is also known as earthnut oil and arachis oil. It is obtained from the seeds of *Arachis hypogaea*, commonly known as peanut. It is largely cultivated on the West Coast of Africa, India, and the United States. The nuts are shelled, the inner red skin separated as completely as possible from the true kernel. The kernels are then pressed. The cold-pressed oil is nearly colorless, has a pleasant flavor and is largely used as a salad oil. The inferior qualities are used in soap making.

Olive Oil. The oil is prepared from the fruit of the olive tree, both by expression and extraction. The commercial product varies from colorless to golden yellow and dark green, according to the variety of tree, degree of ripeness, manner of gathering, and method of expression. "Virgin oil," considered the best quality for edible purposes, is obtained from the

hand-picked fruit, by crushing in such a manner as not to break the kernel. The pulp is then treated with water and pressed again. By this process salad oils are obtained. The pulp is then removed from the press, treated with hot water and again subjected to hydraulic pressure; the oil obtained being employed for lubricating, soap making, and for other technical purposes. The final expression comes into the market as "olive oil foots," extensively employed in the manufacture of "castile" soap

Olive Kernel Oil. This oil is obtained by pressing or extracting the seeds from olive stones. The cold-pressed oil is golden yellow in color, while the hot-pressed oil has a greenish cast. The extracted oil is dark green in color, probably due to the presence of chlorophyll. This oil in a way is the by-product in the manufacture of olive oil, and resembles it very closely in all of its properties.

Animal Oils. These oils are obtained by heating the fatty matter with live or dry steam in open kettles or closed digesters; the old method of heating over the open fire has become almost extinct. One of the most modern processes consists in heating the stock with water, at a pressure sufficiently high to cause a complete separation, but not high enough to decompose the stock. When this "rendering" is complete the contents of the digester is filtered to remove solid matter, and the liquid portion allowed to stand so that the oil may rise to the top. The liquid portion remaining after the oil has been removed, may be used again, or may be concentrated for use as glue stock. The solid matter is usually dried and sold as a filler for use in fertilizers. In some forms of rendering tanks the oil is allowed to rise to the top, where it is removed by tap valves along the side. The oil obtained by the above methods is usually sufficiently pure for commercial purposes. If it is to be used for edible purposes, it is customary to further purify it by bleaching. This is accomplished by passing the oil or fat through bone-black or Fuller's earth.

Animal oils may be divided into two classes:

1. Marine animal oils, 2. Terrestrial animal oils.

Marine Animal Oils. The marine animal oils are characterized by their high iodine values, which in a way resemble the vegetable drying oils. As with vegetable oils, we have a gradual lowering of the iodine value through drying, semi-drying, and non-drying oils, until we approach the constitution of the terrestrial animal oils. The members of this class of oils are liquids at the ordinary temperature, and will be considered under the three following groups:

Fish oils Liver oils Blubber oils

Fish Oils. The fish oils are obtained from various parts of the body of such fish as menhaden, herring, sardine, salmon, etc. The fish, or oily portion is placed in rendering tanks, boiled and the oil drawn off from the

top. The soluble portion is used for making fish glue, isinglass, and the solid portion sold as a fertilizer under the name of fish scrap.

TABLE OF CONSTANTS FOR SOME COMMON FISH OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Menhaden........	0.927–0.933	15.5°C	190.6	139–173	1.480	15°C
Sardine...........	0.933	15 °C	......	161–193	1.479	15°C
Salmon...........	0.9258	15.5°C	182.8	161.4	....	....

Menhaden Oil. This oil is prepared from the body of the fish, which in appearance resembles herring, although it is somewhat larger. From May until November large quantities of these fish are caught off the New Jersey Coast. The fish are brought in by the fishing steamers, and delivered directly to the boiling pans. The resulting oils come into the market as: " prime crude," " brown strained," " light strained," "bleached winter oil," and " bleached winter white oil." Its principal use is in the currying of leather, and in the manufacture of degras and sod oils. It is also employed as an adulterant for cod liver oil, and is used to a limited extent in paint.

Sardine Oil. This oil is obtained in the preparation of canned sardines. It is also made on a large scale in Japan by chopping the fish and subjecting them to boiling and pressing.

Salmon Oil. This oil is obtained on a large scale as a by-product in the canning industry of British Columbia. It is of a pale golden yellow color, with very little odor, and not unpleasant taste.

Liver Oils. As the name implies, these oils are obtained from the liver of various species of fish. They form a natural group which is characterized by the large amount of cholesterol, and other biliary substances present in them. The iodine values bring them between the fish and blubber oils.

CONSTANTS FOR LIVER OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Cod liver.........	0.9210–70	15°C	171–189	167	1.4800–52	15°C
Haddock liver.....	0.9298	15°C	188.8	154.2	....	....
Shark liver.......	0.9163	15°C	161	114.6	....	....

Cod Liver Oil. There are many grades of cod liver oil on the market, obtained in various ways from the liver of the cod fish. The purest form of oil for medicinal purposes is that prepared from fish which are brought ashore alive. The livers are heated in jacketed kettles, the resulting oil being known as " steamed liver oil." When it is impossible to bring

in the live fish, they are opened and the livers collected. Provided no decomposition has taken place the oil obtained from this stock is known as "pale cod liver oil" and is used to some extent for pharmaceutical purposes. As often happens these livers are landed in a more or less putrid condition, so that the oil from them becomes unfit for medicinal use, and is known as "light brown oil." Should the product become very putrid the resulting oil is known as " brown oil." The oil not suitable for medicinal purposes is used in the currying of leather under the name of " cod oil."

Cod liver oil contains quite an amount of stearine which, to a great extent, settles out on standing. Oils which have been freed from stearine are known as " raked " oils.

Shark Liver Oil. This oil is used to some extent as an adulterant of cod liver oil; it is obtained in a manner very similar to that employed for cod oil. It is also used in the leather industry. The oil appears on the market as " yellow strained," " red," " yellow," " yellow red," " Japanese," " crude," and " refined."

Haddock Liver Oil. The oil from haddock liver closely resembles cod liver oil, to which it is added to quite an extent as an adulterant.

Blubber Oils. Under this heading will be included those oils obtained from the blubber of various fish. They differ from each other quite widely in their chemical composition. In some cases glycerides of non-volatile acids, and in other cases glycerides of volatile acids, thus forming a link between the liquid oils and the liquid waxes.

CONSTANTS OF SOME BLUBBER OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Seal	0.9155–63	15°C	189–196	127–141		
Whale	0.9250	15.5°C	188	121–136		
Dolphin	0.9180	15°C	197.3	99.5		
Porpoise	0.9258	15°C	195			

Seal Oil. This oil is obtained from the blubber of the seal. It varies in quality depending upon the method of extraction, and the length of time the oil has been left in contact with the animal tissue. The following brands appear on the market: "water white," " straw seal," " yellow seal," " and brown seal." The last named oil is the result of long contact with animal matter and extraction at high temperatures.

Whale Oil. Formerly the whale blubber was worked up on board the whaler, but now it is generally brought into the " trying " station. The blubber is stripped from the flesh as completely as possible immediately when it arrives at the works. It is cut into strips, delivered to the melting pan, and boiled with steam. The best quality of the oil is that which melts at the lowest temperature. It is of a pale yellow color, and is known

in the trade as " whale oil, No. 0." On further heating the next quality, " whale oil No. 1," is obtained, which is a little darker in color, and has more of a fishy odor than No. 0. The residue in the pan, together with the flesh of the whale, is heated in a digester under pressure of about 50 lbs. to the square inch. In this way " whale oil No. 2 " is obtained, which is of a brown color, and strong fishy odor. When the bones are worked up an oil is obtained known as " whale oil No. 3." This oil is darker than No. 2 and has a very strong odor. From the flesh which has undergone putrefaction "whale oil No. 4 ' is obtained, this is still darker in color and has a very objectionable odor. The water white and pale brands of whale oil are used for burning, and for soap making, the brown quality being used for leather dressings.

Dolphin Oil. The oil obtained from the blubber of the black fish, in its chemical composition, is intermediate between whale oil, a glyceride, and sperm oil, a wax. There are two varieties of this oil, body oil and jaw oil. Both are of a pale yellow color, and contain large amounts of glycerides of volatile fatty acids. On standing it deposits spermaceti. It is used for lubricating fine machinery; such as watches, and other delicate instruments.

Porpoise Oil. This oil is obtained by boiling the entire tissue of the brown porpoise; it is of a pale yellow color, and consists of the glycerides of valeric, palmetic, stearic, and oleic acids. There are two varieties of the oil, body oil, and jaw oil. It is used as a lubricant for delicate machines.

Terrestrial Animal Oils. The oils of this class have a low iodine number, and therefore, belong to the non-drying oils.

CONSTANTS FOR TERRESTRIAL ANIMAL OILS

Name of Oil.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Sheep's foot...	0.9175	15°C	194.7	74.2	1.4713	25°C
Horse's foot...	0.913–27	15°C	195.9	73.8–90		
Neat's foot....	0.914–16	15°C	194.3	69.3–70.4		
Egg..........	0.9144	15°C	184.4–190.2	68.5–81.6		
Lard oil.......	0.916	15°C	193	73		
Tallow oil.....	0.794	100°C	....	55.8–56.7		

Sheep's Foot Oil. This oil is obtained from the feet of sheep in very much the same manner as described for neat's foot oil, it being similar to neat's foot oil, and is usually sold as such.

Horse's Foot Oil. As a rule this oil is never placed on the market under its true name, but is usually mixed with sheep's foot, or neat's foot oil. What is sold as horse oil is the liquid portion of horse fat.

Neat's Foot Oil. This oil is obtained by boiling the feet of cattle with water. It is of a pale yellow color and free from odor. The commercial product usually contains small amounts of sheep's foot and horses' foot

oils. On account of the high price of neat's foot oil it is often adulterated with vegetable, fish, or mineral oils. The most common adulterants are rape oil, cotton seed oil, corn oil, menhaden or other fish oils, and mineral oil. True neat's foot oil is an excellent lubricating oil, but its chief application is in the manufacture of leather.

Egg Oil. This oil may be obtained by pressure or extraction from the hard boiled yolk of hen's eggs. The pressed oil has a yellow color, while the extracted oil is of an orange shade. The nature of the solvent largely influences the properties of the oil obtained; those most commonly used being ether and petroleum ether. In the form of egg-yolk it has very valuable properties in certain tanning operations.

Lard Oil. This oil is obtained by subjecting lard to hydraulic pressure. The quality of the oil varies greatly according to the pressure and temperature maintained; hence, the constants will vary within a considerable range. Its principal use is as a lubricant, and in cutting oils.

Tallow Oil. The processes of manufacture and the properties of this oil are similar to lard oil. As its name signifies it is derived from tallow.

Solid Fats

Vegetable Fats. To this class of fats belong those which remain solid at the ordinary temperature. They differ, however, very greatly in consistency, ranging from soft to very hard. This variation in hardness is dependent upon the amount of glycerides of oleic and linoleic acids present; the smaller the amount of these glycerides the harder the fat.

CONSTANTS FOR VEGETABLE FATS

Name of Fat.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Cotton seed stearine	0.9188–0.9230	15°C	195	90–103		
Palm oil	0.921–0.9245	15°C	192–202	51.5	1.4510	60°C
Vegetable tallow	0.918	15°C	200.3	28–37		
Cocoa butter	0.9500–0.976	15°C	193.5	32–41	1.4496	60°C
Palm nut oil	0.9520	15°C	242–250	13–14	1.4431	60°C
Cocoanut oil	0.9115	40°C	246–260	8–95	1.4410	60°C
Japan wax	0.9700–0.9800	15°C	217–237.5	4.9–9.5		

Cotton Seed Stearine. This product is manufactured on a very large scale by cooling cotton seed oil, and pressing the resulting solid which separates out. It is of a light golden color, of about the consistency of butter, for which it is used as an adulterant. It is also largely employed as a lard substitute.

Palm Oil. Until recently, the only source of this oil was from the coast of Africa, but at present considerable quantities come from the Philippines. The oil is obtained from the fleshy part of the fruit of the palm tree. The process of making this oil is very crude. Either the fruit is stored in holes in the ground, when by fermentation the oil separates and rises to the top; or, the oil in pressed out by hand. The kernels are not destroyed, and from them palm nut oil is obtained. Palm oil has a pleasant odor, sweetish taste, and varies in color from yellow to dark red. It is extensively employed in the manufacture of soap and in its pure condition is used for edible purposes. The oil is readily bleached by treatment with potassium dichromate and hydrochloric acid, and by blowing air through it.

Vegetable Tallow. From the fruit of the Chinese tallow tree is obtained a hard fat. The fruit is steamed in perforated vessels, in which the fat melts and is run off. The remaining seeds are then pressed and " Stillinger oil " obtained. Another process is also employed in which the whole fruit is crushed and pressed, thus yielding a mixture of vegetable tallow and Stillinger oil.

Cocoa Butter. The cocoa beans are roasted, ground, treated with sodium carbonate and hot pressed. When freshly prepared it has a yellowish color, but it turns white on standing. It has a pleasant odor and agreeable taste, and is used in confectionary, medicine, toilet creams, and soaps.

Palm Nut Oil. This oil as indicated above, is obtained from the kernels of the palm tree fruit. After the fleshy part of the fruit is removed the kernels are collected, screened, ground to a pulp and subjected to hydraulic pressure. It is a white oil, and when fresh has a pleasant odor and nutty taste. It is used very largely for soap making, and in the pure condition it is employed for edible purposes.

Coccanut Oil. Cocoanut oil is obtained from the cocoanut. There are three varieties of this oil in the market, *Cochin oil, Ceylon oil,* and *Copra oil.* The cochin oil is the finest and whitest product. Its superiority is due to the fact that the climate of the Malabar Coast is much drier than that of the other localities where the tree grows, and in Malabar better conditions of cultivation, and methods of manufacture are in use. Ceylon and copra oils are obtained either by pressure or extraction and constitute a large amount of the oil on the market. Cocoanut oil is chiefly employed in the manufacture of soap.

Japan Wax. Japan wax is a hard substance resembling tallow, which is obtained from the berries of several varieties of sumac trees. In its preparation the berries are stored in straw until fully ripened, when they are crushed in hempen sacks. In refining the wax it is pressed through cotton cloth and the hot wax allowed to flow into cold water. When fresh, Japan wax has a light yellow color, but becomes darker on standing. It is used for floor finishes, polishes, and in the currying of leather.

Animal Fats. Under this head are included those solid fats which are derived from animal tissues. They vary in degree of hardness according to the amount of the glycerides of unsaturated fatty acids present, those with the higher amount being the softer.

Although only non-drying fats will be considered it may be well to state that certain animal fats have quite pronounced drying qualities.

CONSTANTS FOR ANIMAL FATS

Name of Fat.	Specific Gravity.		Saponification Value.	Iodine Value.	Refractive Index.	
Horse	0.9189	15°C	200.5	81.2		
Lard	0.934–0.938	15°C	193.5	66.7		
Beef tallow	0.943–0.952	15°C	190.9	46–55		
Mutton tallow	0.937	15°C	193.2–200	38–46	1.4510	60°C
Butter	0.926–0.946	15°C	192–195.2	35–46	1.4510	60°C

Horse Fats. When in a fresh condition horse fat is of a yellowish color, of a buttery consistency, and neutral in reaction. On being allowed to stand for some time it separates into solid and liquid portions. It is now a commercial article owing to the large consumption of horse meat. In some localities it is used for edible purposes in place of lard; its chief use, however, is in the manufacture of soap.

Lard. By rendering the fat which surrounds the kidneys and bowels of the pig a product is obtained known as "leaf lard." This, however, constitutes only a small portion of the product sold under this name. The following grades are recognized in the trade: *Neutral lard No. 1* which is prepared by rendering the leaf in a fresh condition at a temperature of 50° C. This is used in the manufacture of "oleomargarine"; *neutral lard No. 2* which is obtained by rendering the back fat in the same way as No. 1. It is used by confectioners and biscuit makers. *Leaf lard* is obtained by subjecting the residue from neutral lard to steam heat under pressure. *Choice kettle-rendered lard* is prepared from the residue of neutral lard No. 1 by heating it, together with fat from the back, in steam-jacketed open kettles. *Prime steam lard* is the product obtained from other parts of the hog by rendering in tanks by direct application of steam.

Lard is of a pure white color and has, at ordinary temperatures, a salve-like consistency. It is adulterated to a very large extent with beef fat, beef stearine, cotton seed oil, cotton seed stearine, and other vegetable fats. These products are sold as lard compounds, and often so labeled as to give the impression that they are pure leaf lard.

Beef Tallow. The fat from different parts of the animal are, as a rule, not kept separate during the rendering; except when the tallow is to be used in making oleomargarine. In this case the kidney fat (suet) is treated alone. When fresh, beef tallow is nearly white, odorless, and almost

tasteless. The highest grade of tallow is used for edible purposes, but the largest quantity finds application in soap making, lubricating greases, and leather dressings.

Mutton Tallow. As a rule mutton tallow is harder than beef tallow, although in other respects it is very similar to it. The methods of rendering are the same as for beef tallow. Mutton tallow turns rancid on keeping, and hence cannot be employed as a butter substitute, nor used in high grade toilet soaps.

Butter Fat. This product is obtained from the fat contained in cow's milk, and is used entirely for edible purposes.

Butter Substitutes. The butter substitutes on the market consist of mixtures of animal fats and vegetable fats and oils. They are usually colored yellow with annetto or oil soluble yellow. The animal fats are oleomargarine " oleo oil," or neutral lard. The vegetable oils used are, generally, cotton seed oil and cotton seed stearine. In the manufacture of oleomargarine the freshest materials are employed, great cleanliness being necessary. The kidney fat is removed from the slaughtered animal as quickly as possible, carefully selected, washed with warm water, and thoroughly cleaned. This selected fat is then rapidly cooled, cut, shredded and ground in a roller mill. The fat thus disintegrated is placed in tin-lined steam-jacketed kettles and heated to 45° C., at which temperature a portion of the fat separates. The mass is clarified by sprinkling in salt and the liquid portion is run off into shallow tin-lined pans; on cooling the bulk of the stearine crystallizes. The cooled mass is then subjected to hydraulic pressure. The " oleo oil " which runs from the press constitutes the principal raw material for the manufacture of margarine.

The oleomargarine, " oleo oil," is churned with the vegetable oils and fats, and with "pasteurized" skim milk. The object of churning is to overcome the tendency of the oleomargarine to crystallize. From the churn the margarine is run into cooling tanks where it comes in contact with ice water. The solid mass thus obtained is worked in a kneading machine to remove the water, and it is here colored and salted to taste. Many manufacturers also add " butter flavor " which consists of a mixture of propionic acid, butyric acid and caproic acid. This also makes the margerine upon analysis appear more like pure butter.

Liquid Waxes

Sperm Oil. The most important member of this class is sperm oil, which is obtained from the head and blubber of the sperm whale. The head oil, which is the more valuable, when first separated is clear and limpid, but changes to a hard mass on standing. The body oil when fresh is of a light straw color. The two oils are mixed together and allowed to stand for two weeks before refining. The solid portion which separates is removed from the oil by subjecting to hydraulic pressure at 32° F. whereby

a clear oil is obtained known as "winter sperm oil." The press cake is then warmed to about 50° F., and again pressed, thus giving "spring sperm oil." The residue from the second pressing is allowed to stand for several days at a temperature of about 80° F. It is then subjected to hydraulic pressure, whereby "taut-sperm oil" is the result. The oils obtained from these three pressings vary in color from pale yellow for the refined oil to brown in the last named product.

The specific gravity of sperm oil at 15° C. varies from 0.8799 to 0.8835; its saponification value from 125.2 to 132.6; and its iodine value from 81 to 90. It is used as a lubricating oil and in leather finishes.

Solid Vegetable Waxes

Carnauba Wax. Of the vegetable waxes, carnauba is the only one which merits consideration. It is a wax which exudes from the leaves of the *Corypha cerifera*, a palm tree growing in Brazil and a few other South American countries. The white powdery mass which is scraped off from the sun-dried leaves is thrown into boiling water, thus melting the wax which collects as a solid mass on cooling. The crude product is dark in color, but on refining becomes almost pure white. It is very hard and melts at 105° C. It has a specific gravity of from 0.990 to 0.999; the saponification value being from 79 to 95; and an iodine number of 13.5. The principal use of carnauba wax is in candle making, polishing pastes, and for phonograph cylinders.

Animal Waxes

Wool Wax, Lanolin. In the scouring of wool, preparatory to spinning, there is obtained a fatty substance known as "brown grease." The crude product finds application in the currying of leather; while the purified product "lanolin" is used in pharmaceutical preparations.

Beeswax. This product is secreted by the honey bee, and serves as the material for building up the honeycomb. The comb is melted in hot water, strained to remove impurities, and subjected to hydraulic pressure. The press cake is boiled a second time and again pressed. Beeswax is of a yellow color, and practically tasteless.

Spermaceti. This wax occurs in the head cavity and the blubber of the sperm whale. Its method of preparation is indicated under sperm oil of which it constitutes the largest part of the solid portion. In the refined condition it forms white lustrous masses, is very brittle and can be easily rubbed into a powder. Its chief use is in the manufacture of candles.

For a more detailed account of the properties, preparation and uses of oils, fats and waxes consult "Chemical Technology and Analysis of Oils, Fats and Waxes," J. Lewkowitsch, Fourth Edition, 1909, Macmillian & Co.

XXVI

LUBRICATING OILS

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General Considerations. The object of lubrication is to diminish friction and thus conserve power. The shaft does not (or should not) come in contact with its box, but revolves on a thin film of lubricant. I like the conception of Southwick that the shaft rotates on the molecules of the oil as it were upon the balls of a ball bearing. The resistance which the particles of this film offer to being torn apart, or the shearing modulus as the engineer terms it, measures the efficiency of the lubricant employed, consequently the cardinal principle underlying all lubrication is to *use the thinnest (or least viscous) oil that will stay in place and do the work.* Obviously, then, the viscosity or "body" of the oil is of the greatest importance in choosing an oil: this should not be taken at any arbitrary temperature, 70°, 100°, or 212° F., but at the temperature, or between the temperatures, *at which the oil is used.* It often happens that one oil is less viscous than another at one of these temperatures and at the temperature of use the reverse is the case, consequently the other oil should be chosen, in accordance with the principle given above.

Another important consideration to be observed in choosing a lubricant is, that it should not absorb oxygen from the air, forming a gum which would increase the viscosity, or turn rancid, and attack the metals with which it is brought in contact. The liability to oxidize or gum can be shown by the gumming test, which also has been found to be a measure of the extent to which an oil will carbonize in a gas or gasoline-engine cylinder. Besides these two tests, which may be considered as measuring the efficiency of the oil, other tests are employed which either measure the safety, serve to identify the oil, or to determine if it be suitable for the purpose for which it is intended. Such are the flash and fire tests, the evaporation test, the free acid test, and the test for thickeners or soap; while the specific gravity of a mineral oil, iodine and saponification values of an organic oil serve either to identify it or indicate if it be adulterated. The cold test and friction test show its availability under conditions approximating that of use.

Flash and Fire Test. The flash test is the lowest temperature to which the oil must be heated to give off vapors in sufficient quantity, which, when mixed with air, produce an explosive mixture. This temperature in the case of a lubricating oil should not be below 300° F. The fire test is the lowest temperature at which it will give off vapors which when ignited will burn continuously.

Evaporation Test. The evaporation test shows the quantity of oily vapor an oil will give off at the average temperature of the bearing; this quantity should not exceed 5 per cent, and is of importance in two ways. It represents the amount of oil serving its purpose, and of oily vapor affecting the fire risk.

Free Acid Test. The free acid test shows, as its name denotes, the amount of uncombined acid contained in the oil: this in the case of mineral oils is sulphuric, coming from the refining process; with the organic oils it is an indication of age or rancidity and is usually oleic. The amount of sulphuric acid (calculated as SO_3) should not exceed 0.3 per cent; the permissible amount of oleic acid varies according to the purpose for which the oil is to be used; for tallow for cylinder oils not more than 0.15 per cent, for prime lard for signal oil not more than 0.2, and for extra No. 1 lard not more than 1.5 per cent. Free acid in oil attacks the metals of the bearings, journals, cylinders, and containers, and in the case of signal oils chars the wick so that the flame is extinguished sooner than it should be.

Soap Test. Test for "oil pulp," or soap: To artificially and temporarily increase the viscosity of oils—in order to pass specifications—recourse is had to the addition of a small percentage of "dope," "oil thickener," or "white gelatine," a soap, usually oleate of aluminium. This greatly increases the viscosity,[1] causes the oil to chill more easily and to emulsify, thus increasing the friction. Furthermore, it is precipitated by contact with water or steam, causing clogging of the machinery.

Specific Gravity. The specific gravity of an oil when stated as a decimal indicates the usual relation to water; this is commonly employed with the organic oils; the specific gravity of the mineral oils is expressed in degrees of the Baumé scale for liquids lighter than water; here water is 10°, engine oil for example, may be 26°, spindle oil 35°, kerosene 47°, stove gasoline 62°, illuminating gasoline 86°; it is to be noted that the lighter the oil the larger the number on the Baumé scale. These degrees have no connection with the flash point, fire point, or boiling-point of the oils.

Iodine Number. The iodine number or value represents the per cent of iodine absorbed by the oil under fixed and precise conditions: this is quite a definite characteristic of oils, although the very fact they are of organic origin means that the vegetable oils are subject to changing

[1] In a case which came to the writer's notice, the oil would not flow from the viscosimeter at 70° F., required 1167 seconds at 85° and 181 seconds at 110°.

seasons and the animal oils to changes in feed. In the case of olive oil the variation in the iodine number is from 77 to 88; it is impossible, therefore, to express the adulteration of olive oil more closely than about 5 per cent.

Saponification Value. The saponification value indicates the number of milligrams of potassium hydrate required to saponify one gram of oil: as this for most of the oils is about 193 it is no criterion by which to distinguish one oil from another. Its chief value is to determine if an organic oil be adulterated, or compounded with an unsaponifiable one, as mineral or rosin oil.

Cold Test. The cold test is the temperature at which the oil will just flow and indicates the availability of the oil at this temperature. Cases are on record of the stalling of railroad trains and the setting fire to factories owing to the oil freezing in the journal boxes.

Friction Test. The friction test measures the power consumed by the oil. This is carried out upon a bearing as nearly perfect as can be made by mechanical skill and under what may be called ideal conditions —regularity of feed, temperature, and pressure. In performing this test, it should be remembered that the effects of the oil previously used upon the machine persist for about eight hours, even though the shaft and bearing be chemically clean. Consequently reliable readings cannot be obtained until after the machine has run at least this length of time with the oil to be tested.

Choice of Oils for Certain Purposes. R. H. Thurston said, "I have learned not to dogmatize about oils; the only thing to do in any case is to test them and see just what they are good for." By "test" he meant either a friction test or "practical" test. While this is of course true, yet the former is tedious and the latter may involve too much risk, and equally good results for practical purposes can almost always be obtained by the use of brief physical and chemical tests such as viscosity, flash, and specific gravity. Practically the only case where these constants do not hold is where the oil is emulsified with water when used, and here the water seems to exercise a decided influence.

The selection of a suitable oil is determined by the pressure on the bearing per unit area—a square inch—and is independent of the size of the bearing; thus it can happen that the same oil can be used both on a large and a small bearing.

From what has already been said, an oil should be sufficiently fluid to flow readily between a journal and its bearing at the temperature of use, and not be forced out by the pressure under which it is running, or to which it is likely to be exposed; any viscosity in excess of this means a needless waste of power. (Apply the viscosity test.)

The fact should not be overlooked that mineral oils lose their viscosity rapidly when heated, more so than the organic oils, and that the tendency of the latter is to increase the viscosity.

A suitable lubricating oil should not gum or thicken on exposure to the air (gumming test); it should not give off inflammable vapors below 300° F. (flash test); nor lose more than 4 per cent on exposure for a working day at the temperature of the bearing upon which it is used (evaporation test). It should contain no acid to attack the bearing or shaft (free acid test). It should have the least possible cohesion among its own particles and the greatest possible adhesion to the metals of which the shafts and bearings are composed. Petroleum oils fulfill the first condition and animal or vegetable oils the last.

Watch Oil. For oiling the most delicate machinery as watches (and clocks) the oil obtained from the dolphin, blackfish or "snuffer" is used. This exists in the cavities of the jaw and also in the brain or "melon" of the fish; it is rendered at a low heat, chilled and filtered at a low temperature, bleached and refined by sunning in contact with lead plates to remove acid. It is a pale yellow, very fluid oil of peculiar odor.

Spindle Oil. This is the lightest and most fluid of the lubricating oils. The method of preparation of this and other hydrocarbon oils has been given under Chapter XXIII. The gravity varies from 30–35° Bé, the flash from 320 to 390° F., the viscosity 56 to 156 seconds Saybolt at 70° F., and the evaporation test should not be over 4 per cent. From what has already been said, nowhere is the necessity for low viscosity greater than in the case of these spindle oils when the bearings are multiplied by thousands. A case is on record where the increase in the viscosity of the spindle oil stopped the engine and shut down the mill. Besides being used for spindles it is used for sewing machines, typewriters, etc.

Loom Oil. This is merely a heavy spindle oil. One which the writer tested had a gravity of 28°, flash 360° F., and viscosity of 203 seconds. Here, as in the case of spindle oils, the evaporation test should be low, as the hydrocarbon vapors formed have occasioned serious fires.

Engine Oils. Engine oils are classed as light and heavy; besides being used for engines, as their name denotes, they find general employment for shafting, machinery, etc., about the mill or works. They are usually hydrocarbon oils of gravity 32–23°, flash 300 to 400° F., and viscosity from 50 to 400 seconds at 70° F. Where the duty is heavy or the bearings are rough, they are sometimes mixed with animal oils, as lard or whale oils.

Cylinder Oils. Cylinder oils, or more accurately, steam cylinder oils, as the Germans call them, are divided into low and high pressure. Here a different problem has to be met, that of making the oil adhere to the surfaces of the piston and valves. This is accomplished by the addition of some fatty oil which adheres to the metals and the mineral oil adheres to it. The action of the fatty oils would seem to be analogous to that of a mordant in fixing dyes. Pure fatty oils, while they have been,

and may now in some cases (with low pressures) be used, are open to the objection that these, being glycerides, are decomposed by high-pressure steam with the liberation of fatty acids which attack the iron of the cylinder, causing pitting and scoring.

$$C_3H_5(St)_3+3H_2O=C_3H_5(OH)_3+3H\ St.^{1}$$

On the other hand, when the condensed water from the exhaust steam is used as boiler-feed water, owing to the fact that these fatty oils emulsify so well with it, renders it necessary to use pure mineral oils. The cylinder stocks, that is, the pure petroleum bases, have the following characteristics. Gravity 26–28° Bé., flash 500 to 600° F. viscosity 117 to 200 seconds at 212° F. It would seem hardly necessary to state that the low-pressure oil should have the lower of these figures. The viscosity of cylinder oils should be taken at the temperature corresponding to the pressure at which they are to be used.

The fatty oils used are, degras, tallow, linseed, cottonseed, and blown rape, all as free from acid as possible and in quantities varying from 1 to 25 per cent.

A lubricant which seems to promise unusually well for cylinders is an artificial deflocculated graphite suspended in water. This is so fine that it will go through the pores of the finest filter paper and it seems to fill the pores of the metal, ensuring tighter fitting piston rings and at the same time possesses little cohesion.

Gas Engine Oils. Gas engine oils, particularly for the cylinders, should possess as their chief requisite, besides that of lubrication, the property of not carbonizing at the temperatures attained. The liability of carbonization seems to be intimately connected with the amount of tarry matter yielded in the gumming test. For automobiles the oils of the following characteristics have yielded good results. Flash 420–450° F. (covered tester), viscosity 180–185 seconds (at 100° F., Saybolt Universal) gumming tests very slight or slight. For large size gas engines probably a heavier oil would be required having these characteristics;[2] gravity 26–28° Bé. flash 400–475° F., viscosity 250 seconds at 70° F.

Greases. Gillett[3] divides the greases into six classes:

1. The tallow type, a mixture of tallow with palm-oil soap with some mineral oil; this was common twenty years ago.

2. The soap-thickened mineral-oil type, a mixture of mineral oil, usually with lime or sometimes soda soaps, the commonest type at present.

3. Types 1 or 2 mixed with graphite, talc, or mica.

[1] St = Stearic acid = $C_{17}H_{35}COOH$.
[2] Davis, "Friction and Lubrication," p. 121.
[3] *Jour. Ind. and Eng. Chem.*, I, 351.

4. The rosin-oil type, a mixture of rosin oil thickened with lime, or sometimes litharge, with mineral oil. They contain often 20 to 30 per cent of water and are used as gear greases. They may contain also tar, pitch, ground wood, or cork, and any of the fillers mentioned in 3.

5. Non-fluid oils: oils or thin greases stiffened with " oil pulp " or " dope," i.e., aluminium oleate.

6. Special greases with special fillers.

These greases show a high coefficient of friction at first, causing a rise of temperature which melts the grease, producing the effect of an oil-lubricated bearing. The graphite greases show an unexpectedly low lubricating power; the rosin greases show a high friction at first, but after the bearing has warmed up compare well with the more expensive greases. The high moisture content would seem to have the advantage of making them less sticky. The lime soap greases (Class 2) are not as good as the tallow greases (Class 1), and are inferior as lubricants to those compounded with soda soaps.

Greases are in many cases to be preferred to oils, particularly where oil spots from the bearings are to be avoided. They are used upon dynamos, shafting, gears, and where heavy pressure is applied, as in the trains of rolls in rolling mills. The tests applied to greases are much the same as those applied to the oils modified as the differences between the solid and liquid state require.

The following tests are usually applied to the greases: flash, free acid, dropping-point, soap content, free oil or fat saponifiable and mineral, free lime, fillers, and water.

For the flash point a 50 cc. porcelain crucible is used; the free acid is determined as with the oils; the dropping-point, according to Ubbelohde's method, by noting the temperature at which drops fall from a tube of grease surrounding the thermometer and having a standard orifice at the bottom. The soap content is most readily determined by ashing the grease and applying the usual quantitative methods to the ash. The free oil or fat is determined by extraction with gasoline, or if lime soaps be present, with ethyl acetate at room temperature; the oils extracted are examined as described under oils; the free lime and fillers are determined by the usual quantitative methods. Water is best determined by distilling with xylol according to Marcusson [1]. The table on the following page shows the composition of some of the greases.

Belt Dressings. Where the object is the softening of the belt they are usually mixtures of solid fat, waxes, degras, or tallow with fish oils to make the belts cling; in some cases they are mixtures either of corn or cottonseed oils, which have been treated with sulphur chloride, with mineral oil and thinned with naphtha, or they may be mixtures of the above fats with rosin or rosin oil.

[1] Mitt. k. Materialsprüfungsamt., **24**, 48.

COMPOSITION OF SOME GREASES *

Name.	Flash Point, °C.	Melting Point, °C.	Consistence, Gms., 20° C.	Water.	Ca Soap.	Filler.	Mineral Oil.	Fatty Oil.	Free Acid.	Coefficient Friction.
Graphite	195	93	18	tr.	11	16	56	17	0	.097
Sum. motor	160	87	170	tr.	38	....	36.5	25.	tr.	.075
Winter motor	175	86	7	tr.	23	....	40.	37[5]	6.1	.063
K1	193	85	24	0.2	16	....	67.	16.	0	.057
K2	195	93	66	0.3	20	....	60.	20.	0.3	.054
Auto	190	79	11	1.0	19	....	60.	20.	tr.	.046
Tallow	210	52	150†	2.5	..	1.4[1] 2.1[1]	22.	73.5	0	.022
Tallow XX	215	49	200	tr.	..	30.[7]	20.	48.	0	.029
Lead resin oil	240	102	7	24.7	..	1.7[2]	.....	0.	0	.067
Lime resin oil	198	77	31	tr.	..	9.9[3]	.....	0.	0	.048
Lime resin oil	198	75	4	20.0	..	7.8[3]	.....	0.	0	.036
Soda grease	215	83	35	0	..	22.[4]	78.[6]	0.	0	.019
Non-fluid oil	210	76	27	0	9.8	12.9[4]	70.3	7.	0	.026
No. 4 petrolatum	247	47	6	0	..	....	100.	0.	0	.018
Lard oil	265	5	0	0	..	....	0.	100.	..	.011

* Gillett, loc. cit. † Estimated. [1] Potash soap.
[2] Lead soap. [3] CaO. [4] Soda soap. [5] Mainly palm oil. [6] Oil of 24.2° Bé. [7] Paraffin.

Car Oils, Reduced Oils, Well Oil, Black Oils. These are commonly crude oils from which the more volatile portions, the naphthas, and, burning oils, have been removed by distillation or sunning. Some railroad specifications require a gravity of 29° Bé., flashpoint 325° F., cold test 5 to 15° F., according to the season of use, and a viscosity 100 to 120 seconds at 70° F.

Compressor and Ice-machine Oils. These are light spindle oils of a gravity of 26–27° Bé. 60 to 100 seconds at 70° F., viscosity, 325–360° F., flash, and a cold test of 0 to 4° F.

Crank-case Oils. These should emulsify but little with water, consequently should be pure mineral oils Much seems to depend upon the water with which the oil is mixed in the crank case, so it is difficult to predict how oils of practically the same constants will behave with different waters. An oil giving these figures has proved eminently satisfactory: gravity 26–27° Bé., flash 455° F., viscosity 100° at 212° F.

Milling Machine or Soluble Oils. These are usually lard, sulphonated oils, or mineral oils held in suspension by soaps or alkalies, as borax, sodium carbonate; the soaps are either ammonium, sodium, or potassium, with oleic, resin, or sulpho fatty acids. They should not appreciably attack the metals and should form a persistent emulsion. The U. S. Navy requirements are that upon 24 hours' standing upon polished brass, or copper it must not be turned green. German requirements are that a

steel plate, 30×30×3 mm. should not lose more than 18 mg. in a 1 or 2 per cent solution of the oil after lying for three weeks in it.

Neutral Oil. An oil without "bloom," of 32–36° Bé., 290–318° flashpoint and 47 to 81 seconds viscosity at 70° F.

"Oil-dag." This is the term applied by Acheson, the discoverer and maker of carborundum and artificial graphite, to a colloidal suspension of pure deflocculated graphite in oil, so fine that it will go through the finest filter paper. Care must be taken that the oil is free from acid, whether mineral or organic, as this causes a precipitation of the graphite. A small quantity of "Oil-dag" in an automobile oil caused it to last for 700 miles instead of 200, the usual distance with one filling without the graphite.

Oilless Bearings. These are wooden blocks, often of maple thoroughly impregnated with 35 to 40 per cent of grease, which replace metal journals; the grease may be a mixture of paraffin, myrtle, or beeswax with stearine, tallow, or vaseline.

Screw-cutting Oils. These are often mixtures of 27° Bé. paraffin, and 25 per cent fatty oil, preferably cottonseed, although pure lard was formerly used.

Stainless Oils. These are spindle or loom oils mixed with fatty oils —lard or neatsfoot; the fatty oil, being more easily emulsified or possibly saponified in the scouring process, aids materially in washing out the mineral oil with which it is mixed. One type of these oils is compounded of 40 per cent neutral oil, 30 per cent cottonseed, 20 per cent olive, and 10 per cent first-pressing castor.

Transformer Oils. These should be either pure rosin or mineral oils and be free from water, acid, alkali, and sulphur. They may be freed from the first two impurities by treatment with sodium wire after the usual method of organic chemistry They should not lose more than 0.2 per cent when exposed to 100° C. for 5 hours, have a viscosity of about 400 seconds at 70° F., a flash of 340–380° F. and remain liquid at 32° F.

Turbine Oil. Steam turbines require a pure mineral oil of most excellent quality; as the oil is circulated around the bearings by a pump it should be of low viscosity and gravity and free from mechanical impurities. An oil of 30° Bé., 150 seconds viscosity at 70° F., and 420° F. flash has given good results.

Finally, in making out specifications, certain mechanical details should not be overlooked. The barrels should be clean and the oil should be free from specks, dirt, stearine, glue, or anything likely to clog the lubricators that may be used; the oil should be free from tar (still bottoms) as shown by the gasoline test, and if compounded should be composed of oils that mix perfectly.

XXVII

SOAP, GLYCERINE, AND CANDLES

ALLEN ROGERS

Historical. Before the invention of soap, the ancients employed the juice of certain plants as detergents, and also Fuller's earth. The latter was spread upon the clothes and stamped in with the feet. The art of soapmaking, however, is very old, as is proven by the remains of a soapmaker's shop found in the ruins of Pompeii. Early records show that soap was manufactured in Italy and Spain during the eighth century. The first soap works in France was established at Marseilles in the twelfth century, when olive oil was first employed for the purpose of soapmaking. It was during the fourteenth century that soapmaking is supposed to have been introduced into England.

The methods employed in the early days of the industry were very crude, and it was only when Leblanc introduced his process for the manufacture of soda from common salt that the industry made any advancement. It was Chevreul, however, who raised soapmaking from rule-of-thumb methods to a true scientific industry.

Theory of Soap-making. When tallow, lard, palm oil, corn oil, or other fatty material is treated with a solution of sodium hydroxide or of potassium hydroxide, a chemical change takes place, resulting in the formation of a product soluble in water, and possessing properties entirely different from the original oil or fat employed. When the soluble product is treated with an acid the resulting body becomes insoluble. If this operation is conducted in a quantitative manner it will be found that the insoluble substance obtained from the acid treatment is only about 90 per cent of the original weight of the fat. Something, therefore, has been eliminated during the operation. This may be recovered from the mother liquor by evaporation, and is found to possess a sweet taste, an oily consistency, and is known as glycerine. The insoluble portion recovered above has an acid reaction, when combined with alkali is soluble, and upon investigation proves to be made up of such compounds as stearic, palmitic, and oleic acids. Thus we draw the conclusion that fats are composed of glycerides of fatty acids; and that in soap-making the caustic alkali decomposes the fatty glycerides with the formation of salts of the fatty acids known as soap, and the separation of glycerine. This reaction is indicated in the following equation:

$$\underset{\text{Stearic acid in tallow}}{C_3H_5(C_{17}H_{35}COO)_3} + \underset{\text{Caustic soda}}{3NaOH} = \underset{\text{Soap}}{3C_{17}H_{35}COONa} + \underset{\text{Glycerine}}{C_3H_5(OH)_3}.$$

Although there are many substitutes for tallow which are employed in soap-making, they all require caustic for saponification and all act in the manner above described. There are, however, some substances, such as rosin, with which, when used in the production of soap, the action as stated above is modified.

Classification of Soaps. Soaps are divided into two principal classes, namely: *hard soaps* and *soft soaps*. In the former caustic soda is employed and in the latter caustic potash is used. The terms *soda soap* and *potash soap* are also sometimes used to distinguish the two classes. Further, depending upon the method of manufacture, we have *boiled soaps*, *half-boiled soaps*, and *cold-process soaps*. Hard soaps are of various kinds, such as *castile*, *curd*, *mottled*, *yellow*, and *transparent*. Soft soaps come on the market as a paste or in a semi-liquid condition. In some soaps both caustic soda and caustic potash are used in their preparation.

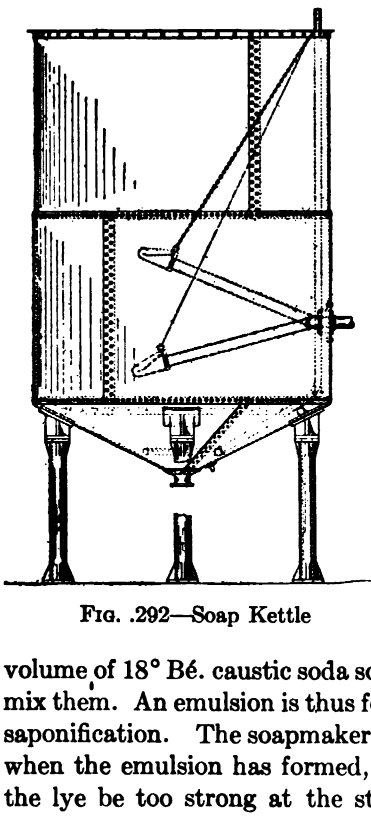

FIG. 292—Soap Kettle

As soap is used for a great variety of purposes, its preparation must necessarily vary. The choice of stock depends upon whether a high-grade toilet soap is to be made, in which the choicest materials must be selected, or whether a cheap laundry soap is to be manufactured. Soap is used very largely in the textile and leather industries, and should be specially prepared for the purpose to which it is to be put.

Boiled Laundry Soaps.[1] The melted fat, usually tallow, is run into the kettle, Fig. 292, together with an equal volume of 18° Bé. caustic soda solution (lye), while live steam is forced in to mix them. An emulsion is thus formed, which is necessary at the start of the saponification. The soapmaker speaks of this as "*killing the stock*," and when the emulsion has formed, the lye has "*caught the stock*,." Should the lye be too strong at the start it does not "*catch*" well, so that it is necessary to add water and continue boiling until the saponification is complete. The point of proper saponification is indicated when a sample removed with a paddle adheres to it and may be drawn out in long strings. Another test is to place some of the soap on the palm of the hand, when it should feel firm and give hard flakes when rubbed out with the finger.

Graining. When the saponification is complete, the soap is "*salted*

[1] The illustrations in this chapter are from Houchin & Aiken, manufacturers of soap machinery, Brooklyn, N. Y.

out" or "*grained*" by adding common salt. This causes the soap to separate from the glycerine and excess of lye, and is complete when a sample taken on the paddle shows a separation into flakes of soap which remain on the paddle while the lye runs off. More steam is now turned on and the heating continued until the soap boils with a broad smooth rolling motion. The steam is shut off and the soap allowed to "*drop the lye,*" or in other words the soap rises to the top, while the lye, containing salt and glycerine, settles to the bottom. The

Fig. 293.—Detail of Perfection Crutcher.

A, Inlet for steam; B, Steam jacket surrounding kettle; C, Outlet for escaping steam and condensation; D, Slip to jacket; E, Space for contents; F, Worm for agitation; G, Case for worm; H, Friction clutch; M, Gate for dumping charge.

pent lye is removed sfrom the kettle and the salt and glycerine are subsequently recovered.

Strengthening. Strong lye is next added to the soap in order to thoroughly complete the saponification, and the boiling continued for two or three days. This second boiling is known as the "*strong change,*" during which time the soap rises in the kettle and may often stand higher than the sides. When the strong lye has caught the stock some rosin is added, and is known as the "*rosin change.*" The amount of rosin

used may vary, but on an average it is about 30 per cent of the weight of the grease. The object of adding rosin is to produce a soap which will lather freely.

Settling. The next step is called "*pitching*" or "*settling*." Water is added to the boiling soap until it presents a smooth appearance, and it is then allowed to rest for several days. The contents of the kettle separates into three layers: the soap at the top, the lye at the bottom, and between them a dark-colored layer known as the "*nigre*." The lye is drawn off into separate tanks and its caustic strength utilized in making up more strong lye. The nigre is allowed to remain in the kettle and increases with each subsequent batch, the soap being drawn off from the top by means of a hinged delivery pipe. When the nigre becomes too bulky it is removed and used for special purposes as, for example, in making cheap tar soap and for some kinds of washing powders.

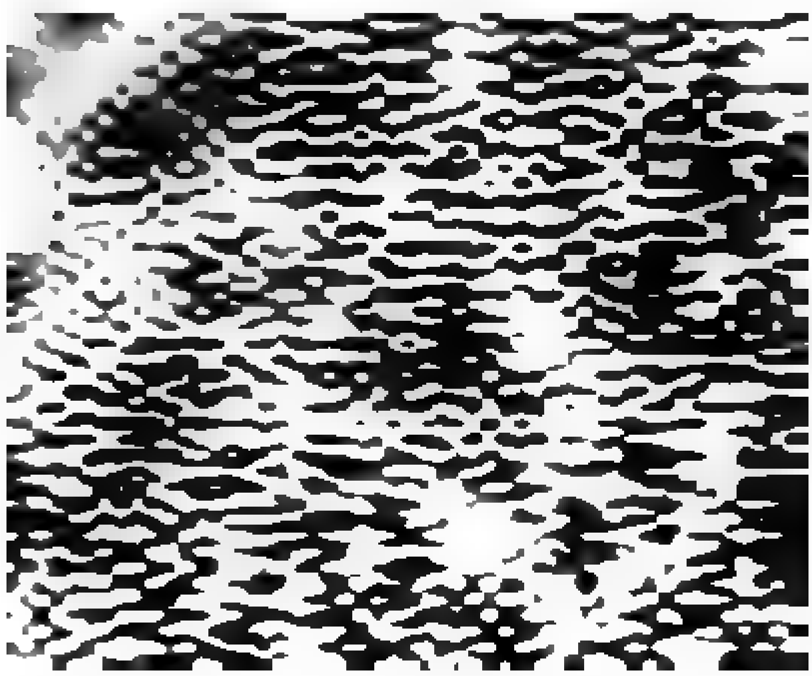

Fig. 294.—Soap Frames.

Crutching. While the soap is still in a liquid condition it is run into the "*crutcher*" in portions of about 1700 lbs. at a time. The crutcher (Fig. 293) is a mixing machine consisting of a steam-jacketed kettle provided with an Archimedean screw, and in the center is a cylinder over which the soap passes during agitation. By this means any perfume or filling material such as sodium silicate, sodium carbonate, borax, and talc may be thoroughly incorporated.

Framing. Having been thoroughly crutched the soap is run into tight boxes or "*frames*" (Fig. 294) supported on trucks and holding the entire charge from the crutcher. In the frames the soap is allowed to set and harden, which usually takes about three days.

Slabbing and Cutting. When the soap has become sufficiently hard to work, the frames are taken apart, and the large cake thus exposed is run through the "*slabber*" (Fig. 295). This is a machine holding a number of horizontal wires arranged in such a manner that the distance between them corresponds to the width of the final cake of soap. The large block of soap, still standing on the base of the frame, is pressed against the wire, either by hand or power, and thus cut into slabs. The slabs are then placed on the "*cutter*" (Fig. 296), also provided with wires, and cut into bars or cakes.

Finishing. From the cutting machine the soap goes to the drying room. When sufficiently dry the cakes are fed into an automatic stamping machine from which they pass to the wrapping and boxing machine.

Fig. 295.—Slabber.

Boiled Toilet Soaps. The method of boiling for toilet soap is the same as for laundry soap, except that a different variety and grade of fat is employed. The raw materials consist mostly of vegetable oils to which a small amount of tallow is added. No rosin, however, is added as the vegetable oils possess sufficient lathering quality. On completion

Fig. 296.—Cutter.

of the boiling operation the soap is run to a continuous drying chamber, where it falls on an endless belt and is slowly conveyed through the drying apparatus, coming out in the proper condition for the subsequent operations. An older method, and one which is still used in many factories, is to crutch, frame, slab, cut, and then "*chip.*" The "*chipper*" (Fig. 297)

consists of an enclosed disk provided with knives which revolve at a high rate of speed, and against which the bars of soap are pressed. The chips thus obtained are dried until brittle and are then ready for the subsequent operations.

Fig. 297.—Chipper.

Milling. Whether the soap has been dried by the modern method or by the slower method of chipping it is placed in a mixing machine where the necessary perfume, color, or other ingredients are added. It is then fed to the "*mills.*" These mills consist of two or more rollers (Fig. 298) between which the soap passes, thereby causing the added material to become well incorporated. The usual practice is to pass the soap between the rollers six times or until the corrugated flakes have a perfectly uniform and smooth appearance.

Plodding. The milled soap is placed in the hopper of a machine known as the "*plodder*" (Fig. 299), where it is subjected to great pressure by means of a compression screw. In the nozzle of the plodder is a "*forming plate*" having an opening the size of the cake desired. The flaky condition of the soap as it comes from the mills is converted into a continuous bar, which may be cut to any length and stamped or pressed as desired.

Fig. 298.—Soap Mill.

Milled soaps allow of the use of delicate perfumes or other materials which would be destroyed if incorporated with the hot soap in the crutcher. The price of a soap depends largely upon the kind of perfume which is used to scent it, as out of the same kettle of soap may be prepared an article selling for ten cents or one dollar. Most good toilet soaps are slightly superfatted so as to overcome the harsh effect of an alkaline condition.

Soft Soaps. Soft soaps are usually prepared by employing potash as the alkali and an oil high in oleic acid as the fatty material. Saponified red oil (see candles) linseed oil, rosin, and cottonseed oil are among the chief oils used for the purpose.

FIG. 300.—Plodder.

Liquid Soaps. These soaps are made in the same manner as soft soaps and are given their liquid property by addition of glycerine or alcohol. Liquid soaps are made from selected stock and the lye well settled before using. Cocoanut oil is largely used for this variety of soap.

FIG. 301.—Bar Cutter.

FIG. 302.—Soap Press.

Half-boiled Soaps. As the name implies, soap made by this process is not boiled. The operation is always conducted in a crutcher, the

temperature of the stock being raised to about 160° F., and the lye added. The mixture of lye and fat is crutched for about five minutes and allowed to stand undisturbed for two hours. It is then crutched again until smooth, tested for excess of either fat or alkali, run into frames, allowed to set and harden as stated under boiled soaps. Half-boiled soaps contain all of the glycerine originally combined in the oil, and for this reason give a very satisfactory soap for toilet purposes. As there is no recovery of the glycerine it cannot be worked economically for laundry soaps. After setting and cooling, it may be chipped, milled, plodded, and pressed in the same manner as boiled soaps.

Cold-process Soaps. Soap made by this process differs from half-boiled soaps in that the oils are only heated to their melting-point and the lye added. The operation is conducted in a crutcher and the mixture stirred until smooth, when it is dumped into the frames.

Floating Soaps. The soaps which float on water are prepared in the same manner as other soaps, and the specific gravity lowered by crutching at a high rate of speed, so as to pump the soap full of minute air bubbles. The same result is obtained by reversing the direction of the paddle several times during the crutching. Floating soap is never milled, but on cooling in the frames is cut into cakes and stamped.

Mottled Soaps. The old-style mottled soaps were made by boiling in a kettle over the open fire and run into frames to cool. During the long process of heating, certain decompositions took place, so that when the soap cooled very slowly the excess of lye and impurities segregated to those portions which were the last to solidify. At present the same effect is produced by crutching with ferrous sulphate, ultramarine, lamp-black, or other pigment just before the soap is run into the frame. Castile or Marseilles soap sometimes have a green mottle, which changes to red on exposure. This is due to the presence of ferrous sulphate, which has been acted upon by the lye to produce ferrous hydroxide; which in its turn is changed to ferric hydroxide by exposure to the air.

Castile Soap. This soap is supposed to be made from olive oil and soda lye only, but as a pure olive oil soap becomes excessively hard and brittle on standing, other oils are usually added. The oils used for this purpose vary, cocoanut, linseed, cottonseed, and corn oil being usually employed. The color of the oil influences the color of the finished product, so that we have both white and green castile soap due to using either a light or colored oil. Practically all castile soap is either made by the cold or half-boiled process.

Transparent Soaps. These soaps are usually made by dissolving a good soda soap in alcohol, decanting away from any insoluble matter and distilling off the excess of alcohol. This leaves the soap in the form of a transparent jelly, which is dried out in moulds having the form of the cake desired. Transparent soaps are also made by the cold or half-boiled process, by adding more glycerine together with a small amount of alcohol

and any perfume or coloring matter which may be desired. A cheaper grade is made by adding a solution of cane sugar.

Shaving Soaps. These are usually soda and potash combination soaps, made from high-grade stock, and are given their strong lathering properties by adding rosin; or they may be made on a cocoanut-oil base with the addition of stearic acid to give body. Many shaving soaps contain glycerine or sugar.

Shaving Creams. These are potash soaps usuallly made on a cocoanut-oil base to which is added a certain percentage of stearic acid.

Toilet Powders. Most toilet powders are composed largely of talc, to which varying amounts of calcium or other stearates have been added. Some powders also contain antiseptic substances such as boric acid.

Soap Powders for Toilet Use. These powders are prepared by completely drying a good grade of toilet soap and subsequently pulverizing it. They must be as near neutral as possible to avoid any irritation when used on tender skin.

Soap Powders for Laundry Use. The trimmings from laundry soap are dried thoroughly, ground to a fine powder and mixed with a certain amount of soda ash. They may also be prepared by adding an excess of soda ash, borax, sodium silicate, or other filler to the soap while it is in the crutcher. Formerly soap powders were ground dry, which was a source of danger and great annoyance to the workmen. Improved processes have recently been introduced by which means the wet soap is fed into one end of the machine and is delivered in a dry and powdered condition at the other.

Scouring Soaps. Soaps of this type are made from laundry stock to which has been added ground quartz (silex), pumice stone, or other abrasive material. The soap is dried in moulds as it cannot be readily cut if allowed to harden in the usual manner.

Scouring Powders. By adding varying amounts of silex, natural earths, or other abrasive matter to a soap powder these products are obtained.

Metallic Soaps. By adding soluble salts of the heavy metals to neutral soap a precipitate of metallic soap is obtained. Some of these metallic soaps have very extensive application in the industries and in pharmacy. The lead soap produced by adding lead acetate to a linseed-oil soap is used as a drier in mixed paints. By boiling olive oil with lead oxide " lead plaster " is obtained.

Glycerine

In former years the spent lye was discarded and by this means a large amount of valuable material was lost. As competition and the demand for glycerine increased, chemists and engineers were called upon to recover this valuable material, and we now have several processes

operating with this end in view. The processes have reached such a stage of perfection that it is almost impossible to find a manufacturer producing a large quantity of soap who does not recover his glycerine either in the crude or refined condition.

The Van Ruymbeke Process. The spent lye from the first boiling and salting out is run into tanks, where any excess of soap rises to the top and may be skimmed off. The clear lye is treated with "persulphate of iron," which precipitates any soluble soap, neutralizes the small amount of alkali, and carries down any nitrogenous matter. Should the lye contain over .2 per cent of caustic soda this must be neutralized with hydrochloric acid before adding the persulphate of iron. The precipitate formed is filter pressed, and the clear, colorless filtrate evaporated under high vacuum. As the evaporation progresses, more lye is introduced in order to maintain a constant level in the pan. During the concentration most of the salt and sodium sulphate crystallize out in a "*salt-catch*" at the bottom of the evaporator. At the end of the concentration the salt is removed through a door in the front and is returned to the soapmaker to be used over again.

When the concentration reaches 32° Bé., the liquor contains about 80 per cent of glycerine and is known as "*crude glycerine.*" Many soap manufacturers sell their product in this condition. To purify the glycerine it is now distilled under high vacuum in a special still containing a closed steam coil, and a perforated pipe through which superheated steam is introduced. The glycerine is carried over mechanically with the steam and on condensing is known as "*sweet water.*" This dilute glycerine is again concentrated until a density of 30° Bé. is reached when it is filter pressed again, and sold as "*dynamite glycerine.*" To prepare "*chemically pure*" glycerine the dynamite glycerine is diluted, treated with milk of lime, bleached, filter pressed, and concentrated.

The Twitchell Process. The object of this process is to separate the glycerine from the fatty acids with which it is combined, so that the latter may be used directly in making soap by the cold process, or employed in the manufacture of candles. The glycerine, being recovered in a concentrated condition, may be marketed without installing the expensive equipment necessary for the other processes.

The fat to be treated is brought to a boil by heating with open steam coil. While boiling, $1\frac{1}{2}$ per cent of 60° Bé. sulphuric acid is added and the boiling continued for two hours. The steam is now turned off and the acid water allowed to settle out by standing. It is of the utmost importance that the waste acid drawn off should not be weaker that 8° Bé., as the stock will not work properly in the next part of the process if the acid water is drawn off too weak. For each 500 lbs. of the washed fat 100 lbs. of distilled water is added. The steam is turned on, the contents of the vat brought to a boil, and the special saponifier added. The boiling is then continued for twelve to twenty-four hours, at the

end of which time most of the glycerine will have been extracted, and the fat should show 85 to 95 per cent of free fatty acids. The glycerine water, which now separates nicely in about half an hour, contains about 15 per cent of glycerine; it is drawn off and a fresh supply of water added. The solution thus formed is treated with milk of lime and the sludge separated by settling or filtration, after which the glycerine liquor is ready to be evaporated to the crude condition or treated by any of the usual methods.

Candles

The principal materials used for candle-making are stearic acid, palmitic acid, paraffin, spermaceti, certain waxes, and sometimes tallow. Candles are made by "*dipping*," "*pouring*" or "*moulding*."

Dipped Candles. The cheapest as well as the oldest method of making candles is carried out by this method. In many of the old New England homes may still be found the relics of the tallow dip, as in our great-grandfathers' days everybody was his own candle manufacturer. The method consists in repeatedly dipping the wick into the melted stock, each layer being allowed to solidify before the next dip.

Poured Candles. This process consists in pouring the melted stock slowly over the wick, which is stretched in a frame. It is only used for wax candles, as this stock contracts so much on cooling that it does not lend itself to the moulding operation. To give the candles a uniform thickness and better appearance they are rolled, while still in a plastic condition, on a flat table with a smooth board.

Fig. 303.—Candle Machine.

Moulded Candles. Most candles are made by this process in a machine, Fig. 303, having a cylindrical metal form, through which the wick is drawn. The stock, while in a melted condition, is poured into the moulds and solidifies around the wick. When cool the casing is removed and the candle finished.

Wicks. The wicks are made of twisted cotton yarn, one thread being drawn tighter than the others so as to cause the wick to curl when burnt. By bending over it is exposed to the air and is consumed, thus obviating the necessity of snuffing.

Preparation of Fatty Acids. The stearic and palmitic acids used in candle-making are prepared by saponification of fat with lime, with dilute acid under pressure, or by means of superheated steam. In all cases the separated fatty acids are chilled and subjected to hydraulic pressure. The liquid fatty acids, mostly oleic acid, which are pressed out, constitute commercial "*red oil*" or "*olein*" employed as a soap stock; while the solid fatty acids known as "*stearine*" are employed as a candle stock.

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XXVIII

LAUNDERING

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Growth of the Industry. The growth of the power laundering industry during the thirty-five or forty years since its initiation in this country has been almost phenomenal. The Census Bureau has never included laundries in the list of industries reported, and as yet no systematic compilation of laundry statistics is available from other sources. However, a conservative estimate,[1] places the number of plants now operated at eight thousand, and the number of employees at 125,000. From these figures it will be seen that power laundering has a much greater commercial importance than is generally supposed.

Among the numerous factors which have made this rapid development possible, the two following may be cited as the most important. First, the marked changes which have occurred in the social and economic conditions throughout the country, and second, the great advances made in laundry practice as a result of the ingenuity displayed by progressive launderers and manufacturers of laundry machinery and supplies.

Most satisfactory results have been obtained in the invention of new kinds of labor saving devices, and it must be conceded that the standard of excellence of the mechanical equipment in the laundries compares favorably with that of other kinds of machinery. Relatively more remains to be done in bringing the chemical side to an equally satisfactory level. Only recently has the value of introducing methods devised in accordance with a knowledge of chemical principles been realized, and in a majority of plants "rule of thumb" methods are still followed.

[1] Editors of the laundry trade journals have furnished these estimates, which are as reliable as can be had. The population returns of the Twelfth Census showed that in 1900 387,013 persons were reported as launderers and laundresses, but this includes others than those employed in power laundries.

Laundries have been included in the 1910 report of the Census Bureau. The number of power laundries given is 5184. This does not include hotel, factory or institutional plants, but it is evident that the figures given in the above estimates are somewhat too large. However, the showing is still a very creditable one.

Nothwithstanding this fact, and in spite of it, the quality of work which can be obtained by the use of machinery and supplies now available and in use is very good. In fact, many laundries do a grade of work that is excellent in appearance and do it with comparatively little injury to the fabrics. It is the small, poorly equipped, and badly managed laundries which are responsible for the prevalence of the notion that the steam laundry at its best is a failure. Although the possibilities in this field have by no means all been realized, much has been accomplished and the future certainly holds much in store.

The practice of doing laundry work in the homes and by the help of washerwomen has become less general, as the quality of the work done by the power laundries has improved. It seems inevitable that the change shall continue at an increasing rate, for the laundries will be enabled to do better and cheaper work, and to observe better sanitary conditions as improvements continue to be introduced.

The laundering industry is not to be classed as a purely chemical industry, but like many others which are largely mechanical, its successful operation depends on the proper combination of mechanical and chemical processes. Besides those chemical reactions which are essential parts of the work, there are others which occur, under certain conditions, as objectionable irregularities. The more extensively the details of both of these classes have been taken into consideration and controlled in a given plant, the more uniform and satisfactory have been the results obtained. For these reasons a brief description of the methods employed in a modern power laundry may not be without interest and value to chemists.

The launderer's business is the cleansing and subsequent finishing for use of textile fabrics, and this is necessarily custom work. For this reason, the methods employed will be different in different localities, but the essential features are quite similar throughout the country. The laundering problem is a complex one, on account of the great variety of fabrics to be handled, and the large number of dyestuffs now used complicates the matter still further. On account of the differences in the chemical properties of the various fibers and dyestuffs, numerous methods of treatment are necessary for the different classes of articles. Those textile fibers most largely used are cotton, flax, wool, and silk, woven either separately or in different combinations. The list of dyestuffs is an extremely large one. For the successful performing of laundry work, a knowledge of the chemical properties of these different fibers and dyes is essential.

Another factor which causes differences in the processes employed is the nature of the substances to be removed and the extent to which the articles are soiled. It is difficult to classify these substances, but roughly, divisions may be made as follows: Albuminous substances, such as blood and egg stains, vegetable dyes which cause fruit and wine

stains; fats and oils, including hydrocarbon greases and oils; acid and alkali stains; body excretions and waste epithelial cells; old starch; street dirt and soot.

For convenience of treatment, the work of the laundry may be divided into several parts. These include generation of power, collection, listing, marking and sorting of the articles, washing, starching, drying, dampening and ironing, followed by finishing and preparation for distribution. It is obvious that many of these operations are not based on chemical principles, and these will be described only briefly, in order that the connection between the various steps may be apparent.

Power Plant. A description of the power plant is not necessary, since it differs in no way from that used for other purposes. Besides the steam generated for driving the engines, large quantities are used for heating ironing machines, drying rooms, hot-water tanks, starch cookers, and various other kinds of apparatus. Use is frequently made of the exhaust steam for some of these purposes, and this effects a considerable saving in expense. Electrical machinery is being installed quite extensively, especially for driving those machines which are used only at irregular intervals. This electrical machinery has the advantage of cheapness of operation and also makes it possible to dispense with overhead shafting and belts, which are very objectionable on account of the dirt and grease they allow to fall.

Marking. After collection, the bundles are brought to the marking room. There they are opened, all articles not already marked are marked with an indelible ink, and a list of each customer's articles is made. Machines operating on the typewriter principle, allow the marking to be done neatly and quickly, and a tabulator, recently invented, makes and prints a correct list of all the articles. The sorting into lots of the same kind is next done, when the articles are ready for the washroom.

Washing Machine.[1] This part of the process is the one which employs chemical reactions more largely than any of the others. The proper handling of the articles in the washroom is absolutely necessary for the turning out of properly finished work, and also for the prevention of excessively harmful action to the fibers.

The machines, Fig. 304, in which the washing is done consist of two concentric wood cylinders (the inner one is often brass) with a space of several inches between them. The outer cylinder is stationary and is connected to the water and steam pipes, and also to the drain pipe. The inner cylinder, into which the clothes are placed through a hinged door, is perforated with a series of small holes, which allows the liquids introduced to partly fill both cylinders. For the purpose of forcing the solution through the fabrics, the inner cylinder is revolved, and an automatic reversing device operates at regular short intervals. All of the solutions

[1] The illustrations in this chapter are from the American Laundry Machinery Manufacturing Co., Chicago, Ill.

with which the articles are treated are introduced into the washer in succession, and the clothes are not removed until they are finished and ready for the extractors, which are centrifugal drying machines.

Detergents. The detergents used are water, soap, carbonate and bicarbonate of sodium and potassium, sodium hydroxide, borax, and mixtures of carbonates and bicarbonates, sold under trade names as washing sodas. In choosing a substance from the list, not only should its action as a cleansing agent be considered, but the possibility of its attacking the fabrics should not be lost sight of. Soaps are unquestionably the best detergents, and the practice of adding large quantities of alkaline substances to them is not a good one, in case a soft water is being used. Neutral soaps, to the solutions of which small quantities of soda ash may be added, are preferable to strongly alkaline soaps, which are generally used in ignorance of their alkaline content. Experiments have shown that soda ash is just as satisfactory as the prepared washing sodas,

FIG. 304.—Washing Machine.

provided it be used properly, and it has the advantage of costing less. Prejudice against the use of soda ash seems to be due to the fact that it is used in too large quantities, since the amount of washing soda called for in the regular formula is simply replaced by a like quantity of soda ash, when a change is made. Since the washing sodas are approximately half soda ash and half sodium bicarbonate (exclusive of the water content) it is seen that a much smaller quantity of soda ash should be taken to give an equally strong alkaline solution. Alkalies react readily with wool and silk, but do not attack cellulose appreciably unless the solutions are concentrated. The chief objection to their use with cellulose is the production of a yellow color, even if the solutions be relatively weak.

Laundry Soaps. The best soaps for general use are those made from good grades of red oil—crude oleic acid. They are much more

soluble than tallow soaps, and the oleates have, in addition, more pronounced detergent action than the palmitates and stearates. This greater solubility is an advantage, since it permits more efficient removal of the soap by rinsing. Resin soaps are inferior as cleansers, and furthermore they produce a yellow cast in the fabrics when used repeatedly.[1]

Theory of Washing. For many years the detergent action of soap has been a subject of much interest to chemists, and consequently a large number of theories has been advanced for its explanation. It is interesting to note that all of these theories, except one published within the last year,[2] start from the same premise, as regards the condition of the substances to be removed, the dirt. According to this assumption, all dirt adheres to fabrics because of a film of fatty substances, and only when the latter is removed is it possible for the dirt particles to be loosened and carried away by the suds. The point of difference between all of these theories, with the one exception, is simply the manner in which this film is thought to be destroyed. Although this cause for the adhering of dirt particles is undoubtedly operative in many cases, it seems very likely that the conclusion that it is exclusively true is unwarranted—it at least lacks experimental proof. Whatever may be thought of Spring's theory, it must be admitted that his experiments show that soap possesses marked detergent properties under conditions where a fatty film is certainly absent. No one of these theories seems to account for all of the known facts, and the problem still lacks an entirely satisfactory solution.

The earliest theory is that of Chevreul, which was published in the report of his researches on animal fats (1811–23).[3] These investigations showed that soap is decomposed into free alkali and acid salts of the fatty acids when it is dissolved in large quantities of water. The alkali thus formed is assumed to be most largely responsible for the detergent properties, which are accounted for as follows: By a simple saponification of the fats by this alkali, the dirt particles are thought to be left free and carried away and prevented from settling in the fabrics by the acid salts of the fatty acids, which constitute the suds. This explanation is an ingenious one, and has for many years been most favorably received. However, there seem to be objections to it which are insurmountable.

It is true that soaps do undergo hydrolysis, but with soap solutions of the strength ordinarily used—only several per cent of soap—the quantity of alkali produced by the reaction is necessarily small, since measurements of the per cent of hydrolysis give small values.[4] Since

[1] H. L. Jackson, Cantor Lectures, 1907; also Dafert and Wolfbauer, *Oester. Chem. Ztg.*, 1908, No. 12, abstracted in *Chem. Abstracts*, 1909, p. 1224.

[2] W. Spring, *Zs. für Chem., und Ind. der Kolloide* IV, 161 (1909), also *Rec. Trav. Chim. des Pays-Bas*, XXVIII (2 série, XIII), p. 120.

[3] Chevreul, "Recherches Chimiques sur les corps gras d'origine animale."

[4] H. L. Jackson, Cantor Lectures, 1907.

saponification at best is one of the slower chemical processes, it is inconceivable that this weak alkaline solution could exert an appreciable action on the fats in the short time necessary for washing. Besides, solutions of the alkalies of the same, or even greater strength, are inferior as cleansers.

A theory which seems to be supported by a larger number of facts assumes that the detergent properties must be ascribed to the emulsification of the fats which are the cause of adherent dirt.[1] The properties which seem to be most closely connected with the detergent action are a high surface viscosity and a low surface tension, both of which are possessed by soap solutions to a marked degree.

Besides the breaking up of the fatty film the power of wetting oily surfaces and of lubricating dirt particles and fibers must be considered important factors in the cleansing process. Hillyer[2] has shown by a number of experiments that these properties also are due to the undecomposed portion of the soap and not to the alkali formed by hydrolysis. A method for grading commercial soaps which is based on this theory, has been devised by Hillyer. The surface tension of solutions of the different soaps against a standard hydrocarbon oil is measured by the drop method. The values obtained classify the soaps in the order of their usefulness as detergents, since solutions having low surface tensions, are shown experimentally to be superior detergents.

As an amplification of the above theory another has been advanced which includes the influence of pedesis, or the so-called Brownian movement, in affecting the size of the dirt particles.[3] Experiments are cited which are interpreted as proving that the bombardment of attached dirt by the microscopic particles in suspension which show the Brownian movement causes a disintegration of the dirt into portions small enough themselves to exhibit pedesis. W. S. Jevons[4] had published a theory which is quite similar to the above, but which did not ascribe as large a part to the emulsification of the fats.

The peculiarity about Spring's theory[5] is that he proposes a new reason for the adherence of dirt particles to fibers, namely, the formation of a dirt-fiber adsorption compound. The explanation of the cleansing action of soap solutions is given by the formation of more stable soap-dirt adsorption compounds, which are carried away by the mechanical action exerted during the washing process. This removes the problem to the field of colloid chemistry, a branch of the science which is just now experiencing a wonderful growth. Although many facts are enumerated in support of this theory, it would seem that it has not assumed its final form, as yet.

[1] Hillyer, *J. Am. Chem. Soc.*, XXV, 511-32, also 1256-65.
[2] Hillyer (l. c.).
[3] H. L. Jackson (l. c.).
[4] W. S. Jevons, *Chem. News*, 21, 66.
[5] W. Spring, (l. c.).

Classes of Fabrics. The nature of the treatment is conditioned by the kind of fabrics being washed, and a number of classes might be made as follows: white collars, cuffs, and shirts, either linen or cotton; colored cotton clothes, usually sorted as to colors; woolen goods; white fabrics other than shirts and collars; and silks. It is evident that all of these groups could not be submitted to the same treatment; as for example, all could not bleached by chloride of lime, as are the white cotton and linen goods. In order to simplify the present description, only the process employed in the case of white linen and cotton fabrics will be outlined and some of its chemical points will be discussed. The main differences between this and the other processes will then be mentioned briefly.

A representative outline of the "collar and cuff" treatment is the following:

	Temperature.	Time of Run.
1. Cold rinse	Room temperature	5 min.
2. First suds	Brought gradually to boiling temperature in 10 to 15 minutes	25 min.
3. Second suds and bleach	Brought gradually to boiling temperature in 10 to 15 minutes	25 min.
4. Warm rinse	60–80° C.	5–10 min.
5. Warm rinse	60–80° C.	5–10 min.
6. Warm rinse and acid	40°	5–10 min.
7. Blue	40°	5–10 min.
8. Rinse	40°	5–10 min.
9. Rinse	40°	5–10 min.

Water Supply. Since water is used throughout the washing process, and is easily the most important agent of all, it may be well in the start to state the conditions which must be realized in a water supply, if good results are to be obtained. Hard water should never be used in the washer. If it is used in making the soap solution, or in the rinses, difficultly soluble soaps of calcium and magnesium, which are difficult to remove, are precipitated in the fibers. If not removed, they make the fabrics harsh, and when heated in the dryroom, or in the ironing machines, they decompose with the formation of yellow or brown substances. Experiments made by the writer have shown that larger quantities of soap and alkaline substances are removed by soft water than by hard, and the color of the finished product is uniformly better in the former case. This is contrary to the belief general among launderers, since when soft water is used, the rinse water continues to form suds even after several changes. This is not due, however, to a removal of less soap in this case, but rather to the fact that by the use of hard water the soap is changed into the above mentioned calcium and magnesium compounds, which do not foam on account of their slight solubility.

The softening must be carefully done, so that the water is left as nearly neutral as possible. Otherwise a larger quantity of alkali must be neutralized when the acid is added, for the sour bath (6), which occasions an unnecessary expense. On account of the large quantities of water used, and since very few water supplies are suitable without treatment, a water softening plant of some kind should be installed in every laundry. It is not difficult to prepare a water which has from three to five degrees of hardness, and which is nearly neutral. An elaborate plant is not necessary —two tanks of suitable size to furnish the water needed are sufficient. Water may be used from one of these, while the precipitate in the other is settling out. The reagents may be mixed with the raw water by stirring with a paddle, with exhaust steam, or with compressed air. Very efficient plants which furnish a continuous supply of water are available. These have the advantage of requiring less ground space per given hourly output of softened water than those of the above described intermittent type. Complete plants of the latter kind, which give perfectly satisfactory results, are also available. In the event that suspended substances are not carried down by the precipitate during the settling, coagulants, such as alum, may be added. A satisfactory procedure is to filter such waters through pressure sand filters which are designed for use in laundries. These filters give very good satisfaction, and are easily cleaned in a very few minutes by simply changing several valves. With an abundant supply of clear soft water good results are made much easier than is otherwise the case.

Cold Rinse. After the clothes are put into the machine, cold water is admitted and allowed to remain for about five minutes. The object of this cold water bath, to which a little soda ash or washing soda is frequently added, is to remove loose dirt, and also to dissolve albuminous substances, which would be coagulated if hot water were used at once. After about five minutes this action should be complete, and the water is discharged.

First Suds. Hot water is now run in, and the soap solution containing the alkaline substances, if any are to be added, are introduced. By admitting steam from the boiler, the temperature of the water may be raised to about the boiling point and kept there during the remainder of the run. The quantity of soap and alkali added is varied with the conditions, an average being sufficient to make the strength of solution about $\frac{3}{4}$ per cent in soap, and $\frac{1}{4}$ per cent soda ash. For a machine designed to wash 75 lbs. (approximately) of air dry clothes, about thirty gallons of this solution are required. After twenty-five minutes the solution is discharged. A very good feature would be to rinse at this stage in order to remove the dirty soap solution left in the clothes.

Second Suds. The second soap and alkali solution is generally made a little weaker than the first. The bleach liquor is added along with the soap, and the whole discharged after twenty-five minutes. The bleach

most frequently used is sodium hypochlorite made from the calcium salt by treatment with soda ash. Electrolyzers for the preparation of sodium hypochlorite from common salt solutions by electrolysis are being introduced into some of the laundries. The bleach liquor produced by them is similar in action to that made from bleaching powder and soda ash, as would be expected. The former contains more sodium chloride, but is more easily prepared neutral than the latter. Enough of this bleach solution is added in the washer mentioned above to yield from 50 to 70 gms. of available chlorine. Many colored substances are removed by being oxidized by the hypochlorite, the resulting colorless substances being taken away by the soap and alkaline substances added. Many tests have shown that the available chlorine is all used up in from ten to thirty minutes under the conditions it is used, the difference in time depending on the rate at which the solution is heated. This fact is of importance to launderers, and explains the appearance of a yellow color in certain lots of clothes. The yellow color is caused by the formation of a colored substance through the action of alkalies with oxycellulose, the oxidation product of cellulose and the hypochlorite. The persistence of this color becomes possible when the available chlorine is all destroyed before the solution is discharged. The yellow compound is destroyed by hypochlorites, also by acids.

The most harmful part of the washing process, as it is ordinarily conducted, is unquestionably the bleaching. This has been shown in a number of ways.[1] Independent series of collars have been treated each by a separate one of the operations, e.g., soap, alkali, soap and bleach, acid, etc., and then starched and ironed. Those collars of the bleach series broke much sooner than the others—seven to nine treatments being an average for the bleached collars, and twenty-five for a series washed in hot water and employed as a check. A determination of the breaking strength of cotton threads has shown the same thing.[2] Threads which broke originally at 1725 gms. had their breaking strength decreased to 100 gms. when treated twenty times, using the larger quantity of available chlorine mentioned above.

Acid Rinse. The purpose of the acid solution is the neutralization of all alkalies not rinsed from the goods. The blues which are used to counteract yellowness in the clothes are basic aniline dyes, and are decomposed by alkalies. Sufficient acid is added to neutralize the alkalies and to leave a slight excess—usually less than N/50 with respect to the acid. The acids used are acetic, lactic and oxalic. The first two have the advantage of being very weak acids and consequently do not attack cellulose readily, even when their solutions are concentrated. Oxalic

[1] Unpublished results by writer.

[2] Series of 100 threads each were used in order to obtain a reliable mean value. Duplicate determinations show that the mean thus obtained is accurate within the limit of the other experimental errors.

acid is considerably stronger than these, but is extensively used because it removes iron stains, on account of the formation of complex iron-oxalate anions. The action between acid and cellulose is not marked so long as the acid remains dilute, as is the case while the fabrics are in the machine. However, any acid which is not rinsed out becomes concentrated when the articles are placed in the drying room, or passed over the heated rolls of an ironing machine. Since the acid is not used up during the reaction, a small quantity of this dilute solution is able, after concentration, to hydrolyze considerable cellulose in a relatively short time.

Tests were run on series of cotton threads as follows: the threads were dipped into N/50 solutions of sulphuric, hydrochloric, acetic and oxalic acids. They were then run in an extractor without having been rinsed, and dried for twenty minutes at 100° C. This operation was repeated ten times, rinsing with distilled water between treatments in order to remove the acid left. The following results were obtained:

Original breaking strength	1725
Acetic acid series	1520
Oxalic acid series	265
Hydrochloric acid series	<20
Sulphuric acid series	<20

Fig. 305.—Extractor—a Centrifugal Machine.

Boiling a series of threads in N/50 oxalic acid solution for three hours caused a decrease to 1250. It will be seen that if oxalic acid be used and no rinse follows the blue solution, this operation is one of the most harmful. A series of collars treated in this acid solution with no subsequent rinse were starched and ironed, with the result that after eight to ten times all of them had broken.

Very frequently all of the alkali is not neutralized, and when this is the case the blue does not set evenly. Besides, the alkali causes a

conversion of starch to dextrins and glucose when heated in the ironing machine. These substances decompose at the high temperature into yellow products, a fact which often explains the production of poor work under these conditions.[1] From the washer the articles are placed in large centrifugal machines, Fig. 305, which are driven at a speed of 1700 to 2000 revolutions per minute. This removes most of the water in about fifteen to twenty minutes, so that the fabrics are in a suitable condition to be starched at once.

Starching. Starching is done in machines which rub the solution into the fabric. The starches most extensively used are the so called thin boiling wheat and corn starches. They have been partially converted by acids, according to the processes given in Chapter XXXIII, until they

FIG. 306.—More recent dry rooms are provided with an endless traveling belt, to which the fabrics are fastened. The speed of this conveyor is regulated so that the articles remain in the dry room about half an hour. Upon emerging from the dry room, each piece is automatically released, and falls into a basket.

form a relatively thin solution upon being boiled with water. The solution is used hot, from 65–70° C., since at this temperature a solution of the strength which gives the right weight and pliability to the finished fabric penetrates most readily (approx. 100 grams starch per liter).

After being removed from the starcher, collars and cuffs are taken to a table where the excess of starch is wiped off, first by rubbing with the hand and then with a piece of cheesecloth. Care is taken to get the starch worked into the fabric so that the plies will be held together after ironing.

Since the starcher leaves too much water in the pieces to allow of

Skinner, *J. Am Chem. Soc.* 27, 165 (1905).

their being ironed at once, it is necessary to dry them. This drying is done in specially constructed drying rooms, Fig. 306, which are heated by steam pipes. Ventilation is provided by a system of fans, for the air must be changed frequently in order to remove the large quantities of water quickly. It is not practicable to carry the drying to the extent just suitable for the ironing, so the moisture is removed as completely as possible. It is then necessary to dampen again and this is done by one of several methods.

Dampening. The method used in most small plants, and in many larger ones, is to wrap the collars in damp cloths. Experience teaches the conditions necessary to produce the proper amount of dampening. Machines which work by carrying the articles to be dampened between moist padded rolls are used also.

Ironing. The ironing machines for collars and cuffs, Fig. 307, consist of large gas heated metal rolls, which are padded with cloth, between which the pieces pass. On account of the difficulty of regulating the flow of gas and air to the burners, the temperature of the rolls varies within quite wide limits, and this has a tendency to make the finish of the work irregular. The gloss on the finished pieces is controlled by the friction applied on passing the rolls. Steam heated machines have been perfected in the last few years, and have the advantage of giving more uniform results, since the steam pressure in the boiler is all that needs to be regulated in order to give a certain temperature to the rolls.

Fig. 307.—Collar and Cuff Ironer.

Since collars and cuffs are ironed flat, many of the collars must be turned and shaped. To prevent undue strain during the turning, the seam is dampened by machines, various types of which are available. The shaping is also done by machines, in which the moisture introduced when the seam is dampened is removed, and in some cases the edge of the collar is ironed.

Colored Fabrics and Pieces which Require no Starch. Colored articles cannot be treated with as strongly alkaline solutions as those mentioned above, and the bleaching liquor must also be omitted. It is a common experience that colored articles which are sent to the laundry last much longer than white ones.

For white cotton and linen articles that need not be starched, the usual practice is to take them directly from the extractors to an ironing

machine, called a mangle, Fig. 308, or flat work ironer. These machines have a number of steam heated rolls, between which the pieces pass. They are constructed large enough to iron sheets and table cloths on a single passage between the rolls.

Wool and Silk. Woolen and silk articles must not be treated with alkalies on account of the corrosive action these exert. The chlorine bleach is also dispensed with, since hypochlorites render wool and silk harsh and weaken the fibers very markedly. In case a bleach is necessary, hydrogen peroxide, sodium perborate, or sodium hydrosulphite may be used. All of these substances are obtainable now at a price which permits their use for bleaching wool and silk.

For the ironing of bosoms and cuffs of shirts and plain shirt waists, special machines are used. These have a movable cloth-padded board,

Fig. 308.—Mangle or Flat Work Ironer

upon which the shirt is fastened and caused to pass under a heated roll. Steam heated machines which operate by simply pressing the articles between heated surfaces, are being introduced extensively, and possess the advantages mentioned in the case of other steam heated apparatus. The body and neck bands are ironed by specially constructed machines, which work on the principle of the others already described. Much of the work on fancy articles must be done by hand, and the use of electrically heated irons is facilitating this operation very much.

Cleanliness is very essential in the laundry. All walls must be plain, and all overhead machinery must be arranged so that dirt and oil are not allowed to fall onto the clothes.

Another field for chemistry in the laundry is presented in the analysis of supplies furnished by dealers. Adulterations, such as excessive amounts of water in soaps and starches, talc and water glass in soaps, and common salt and carbonate in caustic soda may be detected, and great savings thus be effected.

XXIX

ESSENTIAL OILS, SYNTHETIC PERFUMES AND FLAVORING MATERIALS

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Historical. The history of perfume materials dates back to the dawn of civilization on the banks of the Indus, the Tigris and the Nile. Sanskrit writers in India two thousand years ago frequently mentioned perfumes.

As the origin of the word perfume shows (Latin *per*-through, *fumare*-smoke) the first perfumes were used in the form of incense, forming a part of religious worship, from the earliest to the present time. It is interesting to note that some of the oldest perfume materials known are still being used. For instance, in ancient India the sacred fires in the temples were perfumed with kusa or kus, the fragrant root of cus-cus or vetiver, a native grass. This odor is a constituent of many of the present popular perfumes, as in the type of ideal and azurea bouquet perfumes. Confucius, the Chinese philosopher, mentions the use of perfumes in China in his works written about 480 B.C. Incense is the most popular form of Chinese perfume to the present time, as shown by the so-called joss sticks or incense sticks, which are imported into this country in large quantities. That perfumes were well known in Babylon and Nineveh is shown by perfume flasks which were excavated by Layard at Nimrud below Nineveh, curious ornamented containers of porcelain and glass, with cuneiform inscriptions. In Egypt perfumes were lavishly used in the form of incense, as fragrant ointments and oils, in daily life as necessary toilet accessories, as part of the religious ceremonies and in the preservation of dead bodies, which was therefore called embalming. In early Greek and Roman writings, as well as in the Bible, we find frequent references to perfumery and incense. All these ancient perfumery materials consisted of crude drugs, flowers, herbs, aromatic gums, resins and woods of the Orient, including many of the fragrant flowers, which are utilized in modern perfumery. The earliest method of extracting the odorous constituents from the crude material consisted of maceration in oil. The ancients knew that fats have the power to take up and

hold the perfume of substances with which the fat is brought into contact. This old process is still followed in southern France, where flowers are macerated in oil to produce the so-called "flower pomades." The Greek writers Appolonius and Theophrastus mention many of the flowers and materials found in commercial application up to the present time, among them iris or orris, lily, rose, violet and labdanum, an Oriental gum, the active principles of which have lately come so prominently into use as a fixative in the manufacture of fine modern perfumes. Inasmuch as all the materials first used—that is, resins, barks, woods, herbs, flowers, etc., contain the fragrant principles in only very minute proportions, great bulk had to be used and the next step forward was the discovery of steam distillation. The forerunner of this method was the crude attempt of the ancients, who noted that the steam from a boiling caldron had the odor of the contents and who placed wool over a vessel in which for instance, cedarwood was boiling in water, and then squeezed the wool in order to obtain the condensed volatile oil.

While the Egyptians were said to have been acquainted with the principles of distillation, nothing positive is known. Avicenna, a famous Arabian physician and writer of the tenth century, is said to have perfected the process, and the Arabian word alembic (meaning *al-* the, *embic-* still) is used even at present. It is likely he produced the first rose water and rose oil by steam distillation, a commercial process by which oil of rose is now made in Bulgaria.

In time it was found that the odor of most substances which are useful in the perfumery industry is due to a certain class of bodies designated under the terms of essential or volatile oils. Some of these may be obtained from the raw materials by steam distillation, that is, steam is passed through a mass of the flowers, herbs, seeds, woods or barks, which frequently must first be finely subdivided or ground and on cooling the steam, the oil, which is volatile with it, separates from the condensed water. In a few cases, as with rose and orange flowers, the condensed water is likewise salable, because it contains the more soluble portions of the flower odor in solution, although only in infinitesimal quantities. Steam distillation is commercially used in producing a number of the essential oils, for instance, anise, cassia, clove, geranium, lavender, linalœ, neroly, orris, peppermint, rose, sandalwood, turpentine, wintergreen and ylang ylang. From the small alembic used in former times to a modern still which has a capacity of many thousands of gallons, there has been no change in the principle.

Crude Distillation. Many of the essential oils are distilled by unskilled natives in the various countries and the layer of water is usually heated by direct fire placed under the still. It is now well known that this both decreases the yield and produces an oil inferior in quality, as it subjects the material to the saponifying or hydrolizing influence of hot water and some small particles of the substance being distilled are sure to adhere to

the bottom of the still, where they scorch, and contaminate the distillate with a burnt odor.

Modern Distillation. In modern factories steam is generated in a boiler and passed into the still at various degrees of pressure. Usually the still is also heated either by means of a steam jacket or by a closed steam pipe placed inside the still, so as to prevent much condensation of the steam in the still. The degree of fineness of the charging material, the pressure, and therefore the temperature of the steam, the speed of its flow and numerous other working points must be adapted in each case to the apparatus in use, as well as to the substance that is being distilled and the product that may be expected.

Oil Content. The volatile oil content in plant material differs enormously. For instance, cloves contain from 14 to 20 per cent of oil. As a rule, however, most of the plants contain less than 5 per cent and in many cases, only the merest traces of essential oil. It may be mentioned that it requires over 4000 lbs. of rose flowers to obtain 1 lb. of pure rose oil by steam distillation.

Steam Distillation. Oils obtained by steam distillation, however, cannot be expected to have the exact odor of the flower or material. We must remember that the odor and taste of all natural products are due in almost every case to a combination of a number of chemical bodies and it is only when these chemical individuals are assembled in the right proportion and combination, that the odor of the flower or material will be duplicated. Many of these chemical bodies are extremely sensitive to heat, which either destroys them or changes the odor completely, others are esters which are hydrolized by the action of steam and heat and many plants contain bodies which upon heating act to a greater or less extent on the other constituents. Consequently, steam distillation has its limitations and other processes must be utilized to extract the active principles desired.

Scientific research has also proven that many plants contain bodies of very high boiling-point, which influence the odor considerably and which are at best only incompletely volatilized by steam distillation and frequently remain entirely in the residue. Some of the valuable constituents do not exist in the plant as such, but are combined as glucosides. As instances we may mention the odor of cumarine, so apparent in mown grass and entirely different from the odor of the field, and the odor and flavor of vanilla beans, which is developed in the fruit on ripening, but to a far greater extent when the bean is skillfully cured.

Expressed Oils. That squeezing the rinds of some fruit left a fragrant oil on the hands must have been early observed. It is still the method which gives the finest oils of the citrus family and is the present commercial method of obtaining the oils of lemon, orange and bergamot. As cheap labor is available in Sicily, where these oils are made in quantities, and the pulp of the fruit is worked up for citric acid, the price

remains quite low, although the method is slow and tedious. The peel is manipulated, crushing the oil cells and the oil is absorbed by a sponge, which is then squeezed and the oil filtered for the market. Machines have at times been tried to take the place of hand labor, but none of them have been found commercially satisfactory, excepting to a limited extent for the regularly shaped bergamot. The citrus oils will illustrate the damaging influence of heat and steam on odors in general, as steam distilled oils totally differ in odor from the fruit and have but little commercial value.

Macerating Process. We have already mentioned the process of macerating flowers in warm oil or fat, a method by which the modern flower pomades are produced in southern France. After the oil or fat has absorbed the odor of the flowers, it is strained off and a fresh lot of flowers added. This process is repeated a number of times, according to the strength of pomade desired.

Enfleurage Process. It was found, however, that even the slight heat necessary in the macerating process is sufficient to destroy some of the more sensitive constituents of some flower odors, and the cold enfleurage process resulted. Here a layer of fat is placed on a plate of glass, fresh flowers are sprinkled on it and after the fat has absorbed the odor, they are replaced by more flowers and this process is repeated until the fat is saturated. This process is especially adapted to flowers like the jasmine blossom, which is known to produce perfume for some time after it has been picked and a much better yield results than when the flower is immersed in hot fat, which immediately stops the production of more flower oil by the blossom.

Flower Pomades. This flower pomade, obtained either by maceration or by the enfleurage process is then washed with alcohol, which extracts from the pomade the odorous substances, which this has absorbed from the flowers. Here again the same objection of large bulk presents itself, as the fat absorbs only a very small proportion of the fragrant constituents. Then there is another more serious objection to the flower pomades that are obtained by maceration or enfleurage, namely, that the fats employed (usually lard or tallow) will turn rancid in time and furthermore, even the best quality of fats contain a small proportion of alcohol soluble constituents which impart a greasy odor to the spirit used for washing the pomade. This greasy by-odor, (and, where pomades have been kept for a long time, the decidedly rancid by-odor) seriously interferes with the flower odor proper.

Volatile Solvents. These objections have led to the more modern process of treatment by volatile solvents. Petroleum ether, carbon tetrachloride, chloroform and other volatile bodies have been used for this purpose. These solvents in passing through a layer of flowers or materials, dissolve the odorous constituents, together with the plant resins, coloring matter, waxes and other substances. By then distilling off the sovlent

at a low temperature, the odorous bodies with the impurities mentioned, remain in the residue. To this wax or paraffine are usually added to reduce cost and to give a uniform consistency.

Flower Concretes and "Absolutes." By this method, the so-called " flower concretes " are made in southern France. This process has recently been improved again by eliminating from this concrete the alcohol insoluble portion. The concrete is treated with alcohol, thus extracting only the alcohol soluble constituents and the alcohol distilled off, which gives a final product, marketed under various trade names, but usually called " absolute flower concrete " or " absolute flower essence." In another process, the waxes naturally present are precipitated, separated, and the solvent then evaporated in the usual manner. So-called " absolutes," however, are far from absolute in practice, because they still contain quite a large proportion of coloring matter and odorless constituents present in the plant—furthermore, it is quite a common practice to add to these so-called " absolutes," comparatively odorless esters or oils, with the two-fold object of making the products more soluble and of reducing their cost, or increasing the profit in marketing them.

Adulterations. Owing to the high value of many essential oils and perfumery products, they are frequently adulterated. In former years, this was very crudely done by adding paraffine, fatty oils in varying proportions, alcohol and other crude diluents. As science progressed, however, and made many methods available for testing the purity of these products, these clumsy adulterations have gradually disappeared from the market. But their place has been taken by much more dangerous adulterants, which frequently can be found only by careful analysis. For instance the odorless ethyl citrate has found its way into many essential oils which are valued according to ester content and has been used for the adulteration of such odors as bergamot, lavender, etc. While it has been well known for many years that the peasants in Bulgaria frequently sprinkle the rose petals before distillation with either geranium oil or geraniol, more dangerous adulterants have found their way into rose oil, for instance, mixtures of the alcohols geraniol and citronellol, normally present in the rose flower, made so skillfully that their detection in the finished product becomes almost an impossibility. Consequently, many of these oils are valued solely by their odor, when chemical tests fail.

As organic chemistry progressed and methods were found to identify and isolate from the natural materials various constituents present in them, it was found that almost without exception, every odorous material in nature is a compound. Quite frequently materials contain chemical substances or individual chemical bodies belonging to entirely different series and in no way related to each other. Some of these substances are extremely sensitive to heat and chemical reagents and therefore their isolation and identification present the greatest difficulties, but it is just this *combination* of different chemical individuals to which

the fine odor of almost all flowers, plants and other materials is due. As a rule, all of the definite chemical constituents, when used alone, give harsh odors. The delightful flowery aroma is only developed when they are present in proper combination, as they exist in nature, or as the skill of the chemist may combine them. This has led to commercial synthesis of the finer flower products.

Synthesis. The collaboration of thousands of chemists throughout the world, for some years past, has made a new industry possible, the industry of synthetic perfume and flavoring materials, which has come to the assistance of the manufacturer, by producing the same substances at a saving in cost, and by overcoming the frequent price fluctuations of the natural materials, which upset calculations of cost. Many of the substances which naturally exist in the plants or materials, may be manufactured chemically from other sources. Let us select one example, the jasmine flower, which is so invaluable to the perfumer. If we submit the so-called " absolute jasmine flower essence or concrete " to a further process of purification, to eliminate the inodorous constituents present in it, we finally obtain a jasmine essence, which contains from 60 to 65 per cent of benzyl acetate. The absolute product containing this percentage, as made from the blossom, represents an actual expense of about $180 to $200 per pound, according to season. But we can obtain benzyl acetate chemically from an entirely different source, at much less expense. If we take toluene (methyl benzene), one of the constituents of coal tar, and treat it with chlorine, we obtain benzyl chloride. If we now exchange the chlorine for the acetyl group, we get benzyl acetate, which when highly purified, is identical with the product as it exists in the flower and can be marketed absolutely pure, at about $1.10 per pound. This not only represents an enormous saving in the industry, but makes it possible to use raw materials frequently for various purposes, where the natural product was not heretofore available, owing to its high cost.

New Perfume Materials. A great many chemical substances have been found which have most delightful odors and flavors and which, to our best knowledge at the present time, do not exist in nature as such, at least they have not been isolated from the natural materials. Many such substances are now commercially manufactured and have enriched the industry with a variety of new raw materials, which enable the manufacturer to produce entirely new effects. Many years ago, when the industry was in its infancy, and purification processes had not developed to the present state of perfection, the synthetic materials were merely used for the purpose of diluting and cheapening the more expensive natural products, but this has wholly changed during the last few years. The synthetic materials of to-day are successfully utilized in goods of the highest grade and many odor and flavor effects would be impossible without them.

Purification Processes. At the outset, we must emphasize, however, that quality is the foremost consideration in every perfume or flavoring

material. Traces of by-products sometimes present, not large enough to be found by chemical tests, will often seriously interfere with the odro and flavoring value. Modern science has made many methods available by which products may be purified by either chemical or physical methods, so that we can obtain these bodies in a state of absolute purity. Among the chemical methods, we refer to the extraction of aldehydes or ketones by means of bisulphite, semicarbazide, phenylhydrazine and other reagents and the extraction of alcoholic bodies by means of the acid phthalic esters. As one of the most valuable methods of separation we mention the process of vacuum distillation, which has been greatly simplified and perfected during the last few years. Many of the most sensitive constituents of plant odors may be distilled unchanged at a very low vacuum. Scientific advances in engineering practice have so perfected vacuum pumps that substances can be distilled commercially by reducing the ordinary air pressure to an absolute pressure of from 2 to 5 mm., at which point, a great many substances are distilled commercially without change, which would be utterly decomposed if distilled at ordinary pressure. Furthermore vacuum distillation lowers the boiling point enormously, in many cases more than 100° C., thereby reducing heat changes to a minimum, and by carefully repeating the vacuum distillation several times, eliminating in each case the fractions containing the impurities, bodies may be produced in a state of almost absolute purity.

Chemical Treatment. While steam distillation will continue as one of the popular processes of obtaining from some of the plants or crude materials, the active principle, the steam distilled oil can very often be greatly improved by chemical treatment, combined with a proper vacuum distillation process. The natural oils contain many substances which are detrimental to the odor, and can readily be eliminated, in that way producing an article which has a higher perfume value and a much finer odor. As a practical illustration, let us for instance take Mexican linalœ oil, which has a rather harsh and crude odor, owing to the impurities present in it. By chemical treatment and repeated vacuum distillations, we can readily obtain from this oil the valuable terpene alcohol linalool, of which we will speak further on, a product that has a very fine flowery odor and can be safely used in even the highest grade products, where the normal essential oil would be entirely out of the question.

Chemical Constitution. Among the many chemical bodies, which contribute their share to the odor or flavor of materials valued in the industry, we find representatives of both the aliphatic or fatty series and the aromatic or benzene series. The great majority consists of merely three elements, carbon, hydrogen and oxygen. A smaller number of compounds, some of which are important, contain nitrogen—for instance different varieties of artificial musk and amido bodies, derivatives of the benzoic acid series, like methyl anthranilate, one of the most valuable constituents of orange flower and many other flower oils, and the methyl

ester of methyl anthranilic acid or dimethyl anthranilate, which while present usually only in traces, contribute greatly to the flowery sweetness of many of nature's most valued blossoms.

Chemical Methods of Production. The reader will doubtless be interested in the chemical methods used in producing on a commercial scale, by synthesis, the bodies which occur in nature. This however involves so many chemical processes that the subject can only be briefly treated, inasmuch as all the methods of modern organic chemistry are utilized. It may be said for the information of the student, that many of the reactions commercially utilized are exceedingly complex, because the substances in most instances, have to be built up gradually and the intermediary products purified, so that it often requires weeks and months of work to perfect one of the chemical bodies to which a particular flower owes part of its odor. In considering the best known constituents which find commercial application, we shall in a few instances, by way of illustration, mention the process used in their manufacture.

Stability. After producing and purifying the various constituents comes the equally important problem of assembling them in the right proportion, so that they will not only impart the exact odor of the blossom, but will prove commercially stable. Many of these bodies cannot be preserved as individuals—they either oxidize or resinify on exposure to air or light or are condensed into high polymers, which are odorless, therefore of no value and often insoluble in the common solvents. As an instance, let us consider styrol or styrene, which in traces, helps to give life to many flower oils, yet which is of no value alone, as it changes very quickly into meta-styrene, a glassy, horn-like inodorous body, insoluble in alcohol, oils, and all ordinary solvents. Styrol is interesting, as it is one of the few hydrocarbons of value to the industry, having the chemical formula $C_6H_5CH:CH_2$. Berthelot isolated this product from coal tar in 1864, Von Miller from storax. It has not found application until recently, as it was discovered that it would change readily on standing, even when kept in the dark and in sealed tubes. Styrol is merely one example of a large class of substances, which when added to perfume oils in very small proportion produce a natural freshness yet which cannot be marketed by themselves, owing to their instability.

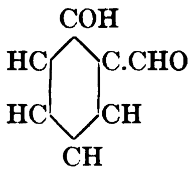
Commercial Synthesis. The student of industrial chemistry, must always keep before him the question—"Is a process feasible—can it be commercially applied?" Owing to statements that have found their way into print during the last decade, many chemists have an idea that by duplicating a few of the major constituents of an odor, they can produce the same effect, but this is false. How often has the writer been approached by a student and sometimes by chemists that have followed organic chemistry for many years, who have expressed their disappointment that for instance terpineol would not produce a lilac perfume or that benzyl acetate would not produce a

jasmine! Here we must remember the complex constitution of materials produced in nature's laboratory. Take for instance benzyl acetate, the item last mentioned—it is well known that in plants, where esters of the acetic acid series exist, esters of allied acids will also be present, though in smaller proportion, and as a rule, we find a mixture of the formates, the acetates, the propionates and sometimes traces of even the higher acid esters in combination with the particular alcohol. Then the alcohol itself, as a rule, does not exist alone. As an illustration, we mention bergamot, which popularly has been supposed to contain only linalyl acetate as the active constituent, until recently, when it was conclusively proven that not only the esters of linalool, but of several of the allied terpene alcohols, are present in varying proportion and unless the chemist who desires to apply synthesis commercially, produces all these different compounds and combines them in approximately the proportions in which nature combines them in the plant, he cannot hope to compete with the products made from the blossom, flower or fruit.

Effect of Minute Traces of Compounds. Scientific investigation has shown that the finest and most valuable odors in Nature, are exceedingly complex. We may find that four or six or ten constituents are present in appreciable proportion and yet if we combine these, the product does not satisfy. The reason is easily perceived—we have ignored the traces of substances present, which sometimes are infinitesimal, but which have such a powerful odor that their addition immediately changes a harsh-smelling compound into a most delicate and flowery product that can be utilized in goods of the highest grade. The higher fatty aldehydes and alcohols, the use of which is but little understood by the average manufacturer of to-day, will serve as an example. Sometimes two or three drops of one of these substances to the gallon, is sufficient to create that life-like touch, or to bring out the charm of the blossom odor to perfection. Many of the most charming plant and flower odors have not as yet been duplicated synthetically, but chemists all over the world are working on these problems and in the course of time, all of the odors will be available, but it must be remembered by the student that he should not be discouraged if he does not get results immediately. It often requires years of painstaking study, in order to ascertain the proportions of individual constituents that will prove of the greatest value and in many cases from sixty to eighty and even more of these constituents are present in a single flower product, although some of them may be present in traces only.

Odor Groups. A great deal has been written about certain odor groups, so called, which are supposed to give definite value when present in a chemical compound. Among these have been mentioned the phenol group OH, the ketone group CO, the aldehyde group CHO, the primary alcohol group CH_2OH or the alkyl radicles as for instance the methyl group CH_3, the ethyl group C_2H_5 and others higher in the series. This is however mere speculation, notwithstanding statements made to the

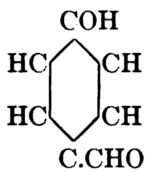
contrary. We should confess that we know very little as yet as to why and under what conditions these groups produce such decided changes in the odor or flavor of a substance, because we have many representative examples, where individual chemical bodies contain either one or several of these groups and yet have practically no odor or flavor. Consequently, we must disagree with the published statements that there is such a thing as advance estimation of a product by knowing its chemical formula. We do know that sometimes the slightest change in a formula, converts a highly odoriferous substance into one that is odorless and vice versa, but we do not know enough about the subject to formulate any theories. In this connection it will be interesting to note that with products belonging to the benzene series, the grouping of the different radicles on the ring, often produces important differences in the physical constants of the chemical body. For instance, let us mention as a typical example, ortho-oxy-benzaldehyde.



Ortho-oxy-benzaldehyde ($C_7H_6O_2$)
(Salicylic Aldehyde)

Here we have the phenol group OH and the aldehyde group CHO adjacent to each other on the benezene ring. It is an oil which has a very powerful odor, is found in traces in many plants and serves as a raw material for building up by synthesis, other compounds, which are valuable.

Let us compare this with the isomeric para-oxy-benzaldehyde, which has exactly the same formula, only here the phenol group is in the para



Para-oxy-benzaldehyde ($C_7H_6O_2$)

position,—that is, opposite to the aldehyde group on the benzene ring. This is a practically odorless white solid, having a melting point of 116° C. This shows that the theory of odoriferous groups works very well on paper, but does not apply in practice, because here we have a substance that contains two of these so-called, odoriferous groups, which has practically no odor, although it can serve as a basis for building up other products by synthesis.

Fixatives. Some of these products which have but little odor are of value to the industry, because they are substances the perfumer calls "*fixatives*." In the plant, the perfume is produced continuously in

mere traces and is given off in infinitesimal quantities to the surrounding atmosphere. When we, however, isolate these bodies to which the odor is due, and have them in concentrated form, their odor as given off is too intense and when we take a small amount of this concentrated material and allow it to evaporate, the odor will not last as long, because it will evaporate more quickly than in the plant and furthermore, the odor being so concentrated and intense, will not be as sweet or as flowery. If we, however, use with the material various substances known as fixatives, the odor is made less volatile. The perfume is only given off in small quantities at a time and we therefore duplicate the conditions existing in nature. In former times, ambergris, musk and some of the resins were extensively used as fixatives, but most of these substances either had such a powerful odor, color or sticky qualities (resins), that they could not always be used in sufficient proportion to entirely satisfy. Here modern organic chemistry has given us a number of substances, which while practically of no odor value themselves are very valuable in combination, because they not only serve as fixatives,—that is, make odors with which they are mixed less volatile, but in many instances have the tendency to sweeten the odor. Among representative instances of this class we may mention methyl anisate, benzyl cinnamate, and benzyl-iso-eugenol, which have but little odor. Synthetic ambergris, the many varieties of synthetic or artificial musk, phenylethyl phenylacetate, mousse de chêne and a great many other products are likewise valuable, wherever their odor harmonizes with the other constituents utilized.

Chemical Groups of Most Importance. If we briefly review the chemical groups of substances which are of most value to the industry, we may mention aldehydes, ketones, phenols, phenolic ethers, alcohols and esters. Esters especially—that is, combinations of alcohols with acids, are frequently of great value as constituents of some of the best known odors and flavors. The acids alone are usually of but little importance. In ester form however, when combined with the various alcohols, they are among the most useful constituents known. This brings us to one aspect of the case, which is of special importance to the chemist who studies for industrial purposes.

Industrial Application. In a great many instances the user of a perfume or flavoring material does not consider the chemical changes or influences against which it may have to contend. All esters are sensitive to alkalies and yet the writer has seen innumerable instances, when, thoughtlessly, perfume materials or flavoring materials that owe their entire value to esters, have been used in combination with alkalies, which will saponify the ester in a very short time and the odor will of course disappear. This illustrates the importance of having the student become acquainted with the individual constituents of either odors or flavors, so that he may use them intelligently and will not employ a product that will decompose under the influences with which it may have to contend and so that either the odor

or flavor may endure. This will also show that care is necessary in selecting an individual material for a certain purpose, to be sure that it will answer and that it will not be destroyed. When we remember that either odoriferous or flavoring materials are used in small proportion only, we realize all the more that chemical incompatibility must be avoided by all means, if we wish to produce an article that will give satisfaction.

Of the crude perfume materials used by the ancients, but few are used at the present time. The animal secretions of value to the industry are very few, namely, musk, civet, ambergris and allied odors.

Musk. Musk is perhaps one of the oldest perfume materials in existence and consists of the dried secretion of the preputial follicles of the male musk deer. This animal has been hunted so excessively that it has become practically extinct and it is now found only in the portion of Asia where the Himalaya Mountains rise to elevations of 8000 to 12,000 ft. Occasionally the animal may wander into lower altitudes, but the greater part of the annual production comes from the Himalaya region. In Siberia we find musk deer, allied in family, but the musk secreted by them is not valued as highly in commerce and does not have as powerful an odor. The musk pods are purchased by native dealers, carried by caravans to the seashore and marketed from Chinese seaports. Commercially the product is known as either Nepaul or Tonquin musk and is now valued at from $20 to $25 an ounce. It is becoming scarcer each year and the time is not far distant, when the musk deer will be extinct, because each musk pod means that a male musk deer has been killed. Of course adulterations are plentiful. The Chinese have excelled in this, and have for many years past sold so-called artificial musk, which is a mixture of dried blood and various other substances, hard to identify, with just a trace of natural musk, marketed at prices ranging from $1 per ounce, upwards. The chemical substance to which musk owes its odor has never been definitely identified. Some research work of recent years seems to point to a ketone, which gives a powerful musk odor, but no chemical work of note has been done on the subject, owing to the high expense involved, and the exact chemical formula of the product is still in doubt. Musk also contains a number of impurities, which rather detract from the true musk odor, but are always present in the natural article.

Synthetic Musk. If we now turn to synthetic musk, we find that here we encounter a product differing entirely in chemical composition, imparting a musk odor and of which many chemical derivatives have been made. The original musk marketed was a trinitro derivative of toluene, and later a trinitro derivative of xylene. This brings us again to the parent substance of so many valuable materials in chemistry and medicine, namely, coal tar. Xylene, which forms a considerable proportion of coal tar, may be condensed with iso-butyl chloride, by means of aluminium chloride, —that is by the well-known Friedel and Kraft reaction, to form iso-butylxylene. After careful purification, this substance is nitrated in the usual

way, by employing a mixture of sulphuric and nitric acids and the final product is thoroughly purified by repeated crystallization. This gives us the artificial musk of commerce, trinitro-iso-butyl-xylene, consisting of small, yellowish, needle-shaped crystals, having a peculiar musk odor. This artificial musk is utilized in many perfume compositions all over the world to-day and while it has not the identical odor of the natural musk, it has replaced it in numerous instances, especially in the soap and perfume industry. The success of these products encouraged scientific research and as a result, a number of other musk compounds have been made which have a stronger and sweeter odor. Among these, we may mention musk ketone, also a nitro product, in which, however, the CO or ketone group is present. Ambrette musk and similar derivatives, made by complicated chemical processes have a more intense odor than any other artificial musk known and likewise have the advantage of being more soluble.

Civet. Civet is the secretion of the civet cat of Abyssinia, where the cat is kept for the purpose of producing a regular supply. It is a substance somewhat similar to musk, but contains derivatives of indol, principally methyl-indol, as its active constituents. As brought into commerce, it is largely adulterated with fats and fatty substances, hairs, clay, etc. The substances present in natural civet, which give it fixative value, have been identified chemically and are produced synthetically. Civet materials are now available, both in liquid and crystal form, as well as the active principle to which the odor of civet is mainly due, namely, one of the methyl indols.

Ambergris. Ambergris is another product belonging to this series and is supposed to be a decomposition product present in the intestines of unhealthy whales. Its use has largely decreased in recent times, as synthetic substitutes have become available at a small fraction of the cost of the natural article, the supply of which is very irregular and uncertain.

Castoreum. Castoreum is a product from the beaver, which has a similar odor to musk.

Gum Benzoin. Of the fragrant gum resins, known to the ancients, but few have survived. Gum benzoin is used in medicine to-day and forms a constituent of many toilet preparations. Sumatra gum benzoin has a dark brown color and a rather disagreeable odor and is only fit for medicinal use,—it should never be employed for perfumery or toilet purposes. The gum coming from Siam or Rangoon is the only variety suited for use in perfumery. It is practically colorless. Gum benzoin is chemically of interest, because from it benzoic acid was first isolated and it has given its name to the chemical benzene or benzol C_6H_6. Then we have gum olibanum or frankincense, and myrrh—Arabian gums of sentimental, rather than practical importance, although used in the manufacture of incense.

Styrax. Styrax from Asia Minor is another gum of decreasing importance, in which, however, important chemical bodies have been found,—among them styrol previously mentioned, as well as cinnamic acid and cinnamic alcohol, both of which are of importance.

Balsam Peru. Then we have the balsam or gum Peru, improperly named because all of it comes from the Republic of Salvador in Central America. This balsam is obtained by crude methods over a direct fire and has a rather smoky odor. It is too sticky to find much application in perfumery and is usually employed in medicine only. There is, however, the so-called oil of balsam Peru, which is separated from the balsam by chemical means, eliminating the resins, which has a very nice odor, although contaminated by the burned smoky smell, due to the phenolic constituents, which result from heating the balsam over direct fire. The product has been analyzed repeatedly and synthetic reproductions are on the market, which are superior in odor to the natural.

Gum Labdanum. Then we have the old gum labdanum, mentioned in some of the ancient works on perfumery, the black color and stickiness of which prevented its extended use. Chemistry has enabled us to isolate from the gum the portion to which the real odor is due, which is now largely employed in the most modern creations and imparts all of the odor value and fixative value of the gum, without the color and stickiness.

Flower Odors. Then we come to the perfumery products, isolated from the flower by means of either the enfleurage process or the maceration process. This group of products includes practically all the finer flower odors, as jasmine, rose, orange flower, tuberose, cassie or acacia, violet, jonquil, hyacinth, mimosa, reseda and a few others of less importance. These flower materials, either in pomade form, as concretes, or so-called "absolutes," have been invaluable to the perfume industry in the past. Very good synthetic reproductions are now also to be obtained at lower cost. In addition we have other flower odors that organic synthesis has made available, which have not as yet been commercially produced from the flower. Among these we may mention trailing arbutus, clover blossom or trefle, cyclamen, gardenia, hawthorn blossom, honeysuckle, the various varieties of lilies, locust blossom, magnolia, melilot, which duplicates the odor of sweet clover, narcisse, new-mown hay, peony, sweet pea, wallflower, and a number of materials which impart the perfume of many kinds of roses. The only two natural rose products which have been available heretofore were either the rose concrete or pomade, made by the cold or maceration process, and the distilled oil, which we shall discuss later. This has a totally different odor from the fresh blossom.

These are merely a few of the successes of organic chemistry which have supplied materials that have not been commercially made from the plants. Many others are manufactured which can also be made from the flowers, but are so produced only to a limited extent, as for instance, carnation pink, hyacinth and lilac.

Chemical Constituents. Many of the finest flower oils contain a number of the same constituents, but in widely varying proportions and influenced by the odor of other bodies present. In the rose we find the terpene alcohols, geraniol and citronellol present in large proportion. These are closely allied chemically. Geraniol has the formula $C_{10}H_{18}O$ and citronell ol, $C_{10}H_{20}O$. Geraniol may be produced more economically from a number of the cheaper oils, as will be shown later. Citronellol has not been found alone but seems always to be accompanied by geraniol. As the commercial separation of these two alcohols is only possible by destroying the greater part of the geraniol present, the use of citronellol alone, which does not exist by itself in the flower anyway, is not advantageous. Under the name of rodinol or rhodinol, a mixture of geraniol, citronellol and isomeric alcohols is marketed, in about the proportion present in the flower. It has a very sweet rose-like odor when perfectly pure and is used in quantities. The esters of geraniol and rodinol, are likewise of importance, the acetates, formates and propionates having a very sweet flowery odor.

Phenylethyl Alcohol Derivatives. Phenylethyl alcohol and some of its derivatives are present in roses and many other flowers. The alcohol itself has a faint flowery odor. Some of its esters are very valuable, the acetate and formate having a decidedly fruity character which imparts freshness to blossom oils containing these esters. The benzoate gives a pleasant odor and also acts as a fixative. Phenylethyl phenylacetate has a very sweet odor reminding one of roses and hyacinths and owing to its high boiling-point, is a very valuable fixative. Phenylethyl propionate also has a fruity character, yet is very flowery when used in traces.

Phenyl Acetic Acid Derivatives. The allied phenylacetic acid has a disagreeable odor, but some of its esters are valuable, both as perfumes and flavors. The ethyl, methyl and benzyl esters are mostly used. The ethyl and methyl esters give a very sweet, honeylike fragrance when used in minute proportion. The benzyl ester has quite a flowery character. We find the phenylethyl or phenylacetic group very widely distributed in many different blossoms, only different derivatives and different proportions are present in each flower. The allied phenylacetic aldehyde is a syrupy liquid when freshly distilled, and has a very strong and pungent hyacinth odor; unfortunately, it does not keep long but changes into polymers on standing. For this reason, it is usually employed in solution in benzyl benzoate or some other solvent, sometimes another aldehyde being used for the purpose. Commercially, the product is known under the name of jacinthe. The instability of this aldehyde, which has such a sweet odor, prompted research work to find some derivative which would have a similar odor but would keep unchanged. Among the many derivatives made, phenyl methyl acetic aldehyde, $C_6H_5CH.CH_3.CHO$, also known under the chemical name of hydratropic aldehyde was found to be perfectly stable. This differs from phenylacetic aldehyde only in so far as one hydrogen is replaced by the methyl group. It has a very

fine and pungent flower odor, which, however, is much stronger in odor than jacinthe or phenylacetic aldehyde. By condensing benzene with any halogen derivative of isopropyl-alcohol, replacing the OH of the alcohol by a halogen by the usual method, iso-propyl-benzene is obtained. After properly purifying the resulting product, we obtain hydratropic aldehyde by oxidation. A number of its derivatives are likewise of importance. For instance, the methyl derivative, readily obtained by using toluene instead of benzene in the above process has an even stronger and more pungent odor,—in fact it is so powerful that the odor is disagreeable, but traces of it produce very pleasing results in blossom oils.

Cinnamic Acid Derivatives. While speaking of materials that have a hyacinth-like odor, we must not overlook cinnamic alcohol, which imparts a very sweet and flowery, though mild, perfume. This alcohol is one of the constituents of gum storax and is present in it as such, as well as in ester form in combination with cinnamic acid as cinnamyl cinnamate, a practically odorless white solid, and also in combination chemically with some of the acid resins of the gum. While cinnamic acid is practically of no odor value, its esters are of value, as they give a fruity effect when used in small proportion and they are present in many flower oils. The methyl, ethyl and amyl esters are the most valuable from the odor standpoint, the first two also being considerably used in the flavoring industry, since when used in traces they assist in duplicating some of the fine fruit flavors of nature. The benzyl ester, benzyl cinnamate, we have already mentioned as a good fixative, although it has very little odor.

Benzyl Alcohol Derivatives. In many of the perfume flowers we find either benzyl alcohol or its esters, which are most widely distributed throughout nature. Benzyl acetate accompanied by the formate and propionate is an invaluable constituent in jasmine, of which indeed these esters form the bulk. The same compounds may also be found in tuberose, ylang ylang and many other of the oils previously mentioned. Benzyl alcohol is easily prepared, because by chlorinating toluene we form benzyl chloride and by exchanging the chlorine for either the hydroxyl group or for one of the acid radicals, we may obtain at will, either the alcohol or any ester. Any of these esters may of course also be made from the alcohol and some of them are so prepared by condensation in the usual way. Benzyl acetate has a very fruity odor and has found much favor itself, as a soap perfume, in combination with other synthetic substances or with some of the distilled oils. Benzyl formate and benzyl propionate give a totally different odor effect from the acetate. It therefore can readily be seen why flowers that contain a mixture of the three esters will have an entirely different odor from either one alone. On the other hand, benzyl benzoate, the benzoic acid ester of benzyl alcohol, has only a slight odor, but is highly valued as a solvent and as a cheap fixative. It is extensively used for dissolving artificial musk crystals. While it requires

about 12 to 14 pints of spirit to dissolve an ounce of artificial musk, this amount is freely soluble in 4 ounces of benzyl benzoate and may then be mixed with other oils in any desired proportion. Benzyl benzoate also has been used to some extent as a fixative in flavors, as it makes the more volatile flavors permanent, especially in cases where the flavor has to stand prolonged heating, as in the confectionery industry, in making chewing gum, and for other commercial applications.

Benzoic Acid Derivatives. While the benzyl ester of benzoic acid has so little odor, both the methyl and ethyl esters of benzoic acid have very powerful odors. The methyl ester is used extensively in the soap industry under the trade name Oil of Niobe. The ethyl ester is used more often as a flavor and when properly employed, imparts characteristic freshness to many of the fine fruit oils. Some of the derivatives of benzoic acid are likewise important. For instance, ortho-amido-benzoic acid, which has the same formula as benzoic acid, excepting that one hydrogen in the ortho position to the carboxyl group is replaced by NH_2, is the parent substance for both methyl anthranilate and dimethyl anthranilate. Methyl anthranilate is the methyl ester of ortho-amido-benzoic acid or anthranilic acid. It is responsible to a great extent for the delightful odor of the orange blossom and clearly shows the inferiority of the steam distilled neroli oil, compared with the orange flower products made by enfleurage or by synthesis. The distilled oil usually contains less than 1 per cent, while the flower product proper contains an average of 10 per cent of this ester. Even in great dilution, its odor value is considerable, and it is more widely distributed than has been commonly recognized because traces of it have been found in many blossoms, while jasmine, tuberose, ylang ylang and other fine flower oils contain appreciable amounts.

If we substitute a methyl group in amido benzoic acid, we obtain methyl-amido-benzoic acid and the methyl ester of this, or dimethyl anthranilate is likewise very valuable. It has a sweet odor in great dilution, which imparts fragrance to many blossoms.

Naphthalene Derivatives. While considering the perfume of orange flowers, which contains so many of the constituents already mentioned, it is curious to note that organic chemistry has also produced an ether of a phenol, a direct derivative of naphthalene, which has the orange flower odor to a great degree,—in fact it is so powerful that the material can only be used in minimal amounts. While the odor is not equal to the flower, it is so cheap and so strong that quantities of this ether are used in soap making and in the cheaper grades of cologne. This is the ethyl ether of beta-naphthol, which may readily be derived from naphthalene. Beta-naphthol condenses very easily with ethyl alcohol and the resulting white or yellowish white crystals melting at 37° C., are known as bromelia or neroline. The latter name, however, has been indiscriminately applied both to the ethyl and methyl ether of beta-naphthol. The methyl ether

has an even more powerful odor, but reminds one somewhat of acacia blossoms rather than orange flowers and has a higher melting-point,—that is, 70° C. The common trade name is yara. Neither one of these ethers has to our knowledge been found in nature and this is apparently an instance where products totally differing in chemical composition have a similar odor, as in the case of natural and artificial musk, which are not related chemically by any means.

Acetophenone Derivatives. Among substances having an orange flower odor, we must not overlook phenylmethyl ketone, known also under the name of acetophenone and hypnone, the last name being due to the fact that some years ago it was extensively used in medicine as a hypnotic. It is a product particularly valuable in soaps, as it is stable against alkalies under all circumstances. Its delightful orange flower-like odor and pungency make it a very valuable addition, not only in many blossom oils but in combinations where proprietary effects are desired. A close chemical relative of this substance is para-methyl-acetophenone, having the same formula, but with a CH_3 group in the para position to the ketone group CO. In commerce this is usually called melilot, although many fancy names have been used. It imparts the sweet honey-like fragrance of sweet clover and gives very similar effects to cumarine, the active principle of the tonka bean. As it is about five times as powerful in odor as cumarine it is one of the most economical perfumery substances known. In soaps it is invaluable as it is likewise absolutely stable against alkalies. Other more complicated chemical derivatives of these substances are also used.

Cumarine. Cumarine is the active principle of tonka beans and is also widely distributed in nature. It is found in quantities in the herb known as deer tongue and in small proportion is present in hay. The odor of new-mown hay in the fields is due partially to this substance. From the chemical standpoint, cumarine is interesting, because it can be made from carbolic acid or phenol, which in turn brings us back again to coal tar which has furnished so many surprises to chemists. Phenol, by treatment with alkalies and chloroform may be readily converted into a mixture of two aldehydes. We mentioned these as an illustration in speaking of the futility of judging the value of a compound by its chemical formula. Ortho-oxy-benzaldehyde is usually formed in the larger proportion and may be readily converted into cumarine by the well-known Perkin reaction, by condensing this aldehyde with acetic anhydride and anhydrous sodium acetate. After proper purification, the chemical so prepared cannot be distinguished from a properly purified cumarine obtained either from deer tongue or from the tonka bean. Purification is of prime importance because the slightest odor of the parent material, or of one of the reagents, adhering to the finished product, will entirely spoil it. Cumarine is largely used in making cheap flavors, also in perfumery and in scenting soaps. Some of its chemical derivatives, the manufacture of which is complicated, are even more valuable.

Benzaldehyde Derivatives. Para-oxy-benzaldehyde is the other aldehyde formed in smaller proportion in the reaction just mentioned. While an odorless solid it can readily be transformed into the methyl derivative, an oil of powerful odor, recalling hawthorn blossoms and known as aubepine.

Salicylic Acid Derivatives. We have just considered melilot as imparting a sweet clover fragrance. The red clover has an odor of its own. One of the main constituents used in duplicating this is a synthetic body, first made in the laboratory and long marketed under various names, as orchidee, sanfoin, etc. This is the amyl ester of salicylic acid or ortho-oxy-benzoic acid. It has about the same relation to trefle or orchidee perfumes as benzyl acetate has to jasmine,—that is, while present in large proportion, its odor is influenced and totally changed by some of the other constituents previously described. Iso-butyl-salicylate has a similar odor and is known under the name of orchidone. Some of the other esters of salicylic acid are likewise valuable. The benzyl ester is used as a fixative and others have found more or less application.

Fruit "Ethers." While speaking of amyl and butyl esters, we should correct a popular error which early found its way into print and has been repeated many times. Over forty years ago it was noticed that the esters of the fatty alcohols and acids had a fruity character. Old formulas have frequently been reprinted, which give the amateur instructions for the manufacture of pear, banana, strawberry and other fruit oils by merely using these esters (called fruit ethers) in combination with chemical substances which should not be used in food products, such as chloroform, etc. When we consider the number of constituents which contribute to the perfume of flower oils, is it to be supposed that flavors which give aroma to the fruits would be less complicated in composition? It is no doubt true that most fruits contain a small proportion of these fatty esters, but they are present very largely as nature's diluent. They bear the same relation to the fruit flavor as terpenes do to oil of lemon or as the odorless benzyl benzoate to the other substances present in flower oils in smaller croportion Hence it requires equal study and care to duplicate synthetioally any of the fruit flavors, after identifying and producing the bodies to which the real fruit aroma is due. Many of the substances present in flowers are also found in fruits. Methyl anthranilate is an example. This material is present in grapes and contributes largely to the flavor. The same is true of phenylethyl alcohol and its esters which are more widely distributed in fruits than is commonly supposed.

Bitter Almond Oil. The essential oil of bitter almond is an illustration of the futility of the classification of essential oils according to their botanical origin. The almond tree is a member of the great Rose family, resembling our peach. There is no difference between the bitter and the sweet almond trees and the fruits of both contain a considerable amount of fatty oil, which is also utilized in medicine, as "oil of sweet almonds." The same oil may be found in the apricot and peach fruit, but in addition,

these two and the bitter almond kernel, contain a body called "amygdalin," which is a combination of glucose, hydrocyanic acid and benzoic aldehyde, and this breaks down into these bodies, when acted upon by a ferment, called emulsin, which is also present in the fruit or seed, or by other hydrolizing agents. After the emulsin has acted, direct steam is applied and a very old process in vogue among the alchemists and named by them "cohobation," is employed. The water which has been distilled off is returned to the still after separating the oil, by which means the total amount of water used is kept down to a minimum and a much larger quantity of oil is recovered. The hydrocyanic acid must be removed from oils intended for flavoring, because it is highly poisonous and during this and the previous handling, care must be taken to prevent, as far as possible, the rapid oxidation of the principal constituent, benzaldehyde, to benzoic acid. This will well illustrate the care which must be taken and the number of reactions involved, in obtaining from nature such a simple body as benzaldehyde, which can be so easily made from toluene. For instance if toluene is treated by chlorine, we obtain according to the proportion of chlorine employed, either benzyl chloride $C_6H_5CH_2Cl$ or benzal chloride $C_6H_5CH.Cl_2$. Benzaldehyde may be made from either of these toluene substitution products. For instance, if we treat benzyl chloride with lead nitrate and water, we obtain benzaldehyde C_6H_5CHO. The oil of bitter almond, deprived of prussic acid, is commercially known as oil of bitter almond, S. P. A. (without prussic acid). The natural oil containing the acid is very poisonous and must never be employed, excepting for medicinal purposes when the prescribing physician specially desires its medicinal effects.

Anise Oil. Anise oil is more easily obtained as it is only necessary to steam distill the seed until the residue is free enough from oil to be used as cattle food. The resulting anise oil is quite complex in composition, the main constituent being anethol, the methyl ether of para-propenyl-phenol and with it is associated the corresponding allyl compound known as methyl chavicol. These bodies are also found in almost the same proportion in an entirely different oil from a botanical standpoint, because anise is a member of the Umbelliferous family, to which carrots and parsnips belong, while the star anise is distilled in China, from the fruit of an ilex tree which is related to magnolia and yields an oil which can scarcely be distinguished by chemical tests from true anise oil. Star anise oil is usually produced in the crudest ways by natives and is sold at a much lower price. The oil is used in medicine and sometimes as a flavor.

Bay Oil. Bay oil is in no way related to the bays or laurels of classical times, but is distilled from leaves of trees native to the West Indies, belonging to the Pimenta or Myrcia family. At an early date, these sweet leaves were soaked in rum and the well-known bay rum was the result. It was later found that an oil obtained by steam distillation, could be added

to alcohol and a very similar product obtained. The oil contains eugenol and methyl eugenol as its principal constitutents. It also contains chavicol and its methyl ether, which has been mentioned previously as present in anise oil, and a little citral, which we shall consider later. In addition there are a number of terpenes, which are bodies that have only recently been investigated and about which we shall have to learn much before we can understand them. They are present in many oils in considerable proportion and in traces in nearly all essential oils that are distilled. They are a disadvantage in practically every instance as they take up oxygen from the air, thicken the oils, give rise to unpleasant odors and have but little odor value themselves. Many of the natural oils contain a large proportion of terpenes and therefore a purified product, which eliminates these, is highly to be preferred in manufacturing, because the purified oil is more soluble, has the odor of the plant or fruit in a higher degree and is more concentrated.

Birch Oil. Birch oil is almost entirely composed of the methyl ester of ortho-oxy-benzoic acid or salicylic acid. This is also the main constituent of value in oil of wintergreen. For this reason, the U. S. Pharmacopœia has recognized artificial methyl salicylate, made by condensing salicylic acid and methyl or wood alcohol. For flavoring methyl salicylate is inferior to ethyl salicylate, which also exists in many natural oils, as the ethyl ester gives not only a sweeter, but more lasting flavor.

Wintergreen Oil. Oil of wintergreen represents one of the few examples of essentials oils that consist of practically one constituent to which the odor and flavor value is due. Almost all the others are more complex in character. Methyl salicylate, mixed with a little ethyl salicylate, can scarcely be distinguished in flavor from the natural oil.

Camphor. Camphor is a body, which, while not strictly an essential oil, is very important, not only on account of its medicinal value, but because it is the parent substance of many other chemical bodies. Japan has controlled its production, but it has also been made by synthesis and artificial camphor is now on the market. Camphor is obtained commercially by distilling with steam the wood of the camphor tree. Recently, the discovery has been made that small plants, just started from the seed, can be mown and distilled with a very good yield of camphor. Camphor is a solid which crystallizes from camphor oil on chilling. Camphor oil, the liquid portion, is very complex and is one of the sources of safrol, which is used commercially in medicine, as artificial oil of sassafras, of which it is the principal constituent. It is also used chemically because by oxidation it yields heliotropine or piperonylic aldehyde, a substance which has a strong odor of heliotrope and is one of the constituents to which the flower owes its perfume. Alone, however, it has but little value and should be reinforced with the other bodies present in the blossom. Heliotropine crystals have proven valuable

as an addition for sweetening soap perfumes and for other technical applications.

Bergamot Oil. The oils of the Citrus family which include bergamot, lemon, lime, orange and bitter orange are all made commercially only in southern Italy and Sicily. All are obtained by expression and not by distillation. Oil of bergamot owes its odor principally to the esters present, consisting of linalyl acetate and allied compounds. The commercial oil usually contains from 30 to 35 per cent of ester and is valued according to ester content. It has been largely adulterated, especially since the price has risen during the last few years and should be purchased from reliable sources. Synthetic products are available, which duplicate the odor at considerably less cost. Linalyl acetate, one of the main constituents of the oil, may also be had at a lower cost, considering that this forms less than one-third of the oil.

Lemon Oil. Lemon oil consists principally (as far as quantity is concerned) of terpenes, which have no flavor or odor value, but which hasten the rapid oxidation of the oil, so that lemon oil will not keep very long and changes into turpentine-like smelling derivatives, which are useless for technical application. The active principles of lemon oil are less than 10 per cent of the whole, the main constituent being citral, the aldehyde of geraniol, which we shall further consider under geranium oil. Citral is usually isolated from lemongrass oil, in which it is present in far larger proportion, ranging from 60 to 80 per cent, according to quality. Lemongrass oil contains, however, constituents that have such a disagreeable odor that the oil itself has found but little application except in laundry soaps. Citral alone even when pure does not produce a fresh lemon flavor. It is well known that other substances are present in small proportion and chemists are engaged in research to duplicate the flavor entirely. Small amounts of linalyl acetate, methyl anthranilate and a number of other compounds are also present in lemon oil. When these have finally been identified and the proportions accurately determined, science will offer to commerce a synthetic lemon oil at lower cost.

Orange Oil. The oils of bitter and mandarin oranges and limes are made on a small scale, but the oil of sweet orange has found extended application in flavors and perfumery for many years past. Oil of sweet orange contains a larger proportion of terpenes, which are useless from the odor and flavor standpoint, than any of the other oils of the Citrus family. In fact it is estimated that less than one-twentieth of the weight of the commercial oil of orange consists of the active odor or flavor-bearing portion—among these decoic aldehyde has been identified as one of the constituents that contributes the main flavor, but many other items are present.

Synthetic Aldehydes and Alcohols. This brings us to the subject of the synthetic fatty aldehydes and alcohols, which are of use in perfumery

and flavors. The lower fatty aldehydes and alcohols containing less than seven carbon atoms to the molecule, are of but little value. Our interest begins with heptoic aldehyde and heptoic alcohol. Both of these may be made from castor oil commercially and have an exceedingly disagreeable odor while impure or while concentrated, but when used in traces prove of high value. Then we come to the eight-carbon atom molecule, octoic alcohol and octoic aldehyde, both of considerable importance in perfumery. They are present in many of our most valued flower oils in infinitesimal proportion. Yet if both of these are utilized indiscriminately, in larger quantities, the result will be failure, because while concentrated, both have a disagreeable odor. Almost the same thing may be said of nonoic aldehyde and nonoic alcohol, both of which are extremely valuable, when used in traces, yet when employed in too large a proportion, the odor effect is entirely out of harmony and spoils the product. Decoic aldehyde and decoic aclohol are of the same importance. As stated, decoic aldehyde is one of the bodies to which orange oil owes its main flavor and odor value. It is a magnificent product when properly used. Decoic alcohol likewise proves of service in many instances, but if used in excess, the effect will be disagreeable.

Duodecoic alcohol and duodecoic aldehyde serve the same purpose. In traces they are valuable. Some instances have appeared in print, where duodecoic aldehyde has been recommended for sweetening ionone and for producing flowery effects when used in the proportion of 10 per cent. Any manufacturer who employs the product in that proportion will be disappointed because if he uses an absolutely pure material, he will find that a very much smaller amount will prove of more service than the larger quantity recommended in the chemical press.

Grass Oils. From the citrus oils, we pass to the East Indian oils of the Citronella family, which includes a number of aromatic grasses. They are known by various names and while closely related botanically, produce oils of entirely different odor effects when distilled. They include the oils of citronella, palma rosa, or East Indian geranium, gingergrass, lemongrass and vetiver. Hundreds of tons of these grasses are distilled annually by the natives in India. Oil of citrionella is mostly used for technical applications and for perfuming laundry soaps. Chemically, it is a source of the important terpene alcohol, geraniol, a constituent of rose oil. It also contains an aldehyde, citronellal, closely related chemically to citral, the aldehyde of lemon oil, which serves as a raw material for building up other materials by synthesis. Oil of palma rosa or East Indian geranium oil is likewise of importance, as it contains a large proportion of geraniol, which is isolated from the oil chemically and finds extended application. The oil itself is used as a soap perfume. Oil of gingergrass, so called, up to recent times was thought to be an adulterated palma rosa oil, but has been proven to be a distinct essential oil, distilled from a different species of grass. It finds application

principally in scenting soaps. Oil of lemongrass is of great value, because this contains, as previously mentioned, a large proportion of citral. Citral is not only one of the active principles of oil of lemon to which the main flavor is due, but may be chemically converted into other derivatives which are of much greater value to perfumery. Citral may be condensed with acetone, by any alkaline condensing agent, forming a ketone derivative known chemically as pseudo-ionone, which by treatment with acids is converted into ionone.

Ionone. Ionone is a direct derivative of the benzene series. The acid treatment converts the chain formula of the aliphatic series into an aromatic derivative, by closing the chain into a ring. Ionone exists in a number of isomeric forms each of which has a slightly different odor. Many derivatives of ionone have been made. The name "ionone" having been trade marked at the time the original patent (now expired) was applied for in 1893, these violet ketones are marketed under various trade names, as iovionol, neoviolone, ional and many others. The conversion of psuedo-ionone by means of acid gives rise to a great many impurities having a disagreeable odor. Consequently, these ketones are on the market in all possible qualities, from those which are almost useless, on account of imperfect purification, to products which have a charming floral odor and are applicable for the finest perfumery purposes. Ionone is an isomer of irone, the active principle of the essential oil or orris root.

Orris Oil. Orris root or the iris of Italy, when distilled, yields an essential oil containing about 90 per cent of myristic acid and about 10 per cent of active perfume substances, of which irone is the main constituent. An absolute orris oil free from the fatty acid is also sold, being from 8 to 10 times as strong. Synthetic orris products also enjoy a large market.

Violet Odors. Ionone, as well as irone, popularly represents the violet odor, but as a matter of fact, many other substances contribute to the violet perfume. The manufacturer who thinks he can get a violet by merely dissolving ionone, irone or orris oil in alcohol is doomed to disappointment, because the other substances are missing, which contribute the life-like character and really produce the complex odor effect which the public knows as violet. Synthetic violet products are available which enable the manufacturer to produce almost any shading of the delicate fresh violet fragrance.

Vetiver Oil. The other related grass oil is the oil of vetiver or cus-cus, but in this case only the roots are distilled. Oil of vetiver is a viscid oil having a very powerful odor and is used in traces in many perfume combinations of the Oriental type. The oil as distilled contains some by-products having an extremely disagreeable odor. A purified product is available which gives a much finer perfume and may be used in larger proportion. It finds employment quite extensively in some of the most modern odors.

Clove Oil. Cloves, one of the earliest items of trade between the East and West, contain such a large proportion of oil that even the crudest methods give a fair yield. Cloves are the dried, unopened flower buds of a beautiful evergreen tree. Clove oil is the commercial source of eugenol which chemically is allyl-methoxy-oxy-benzene. This is present in the commercial oil to the extent of from 70 to 85 per cent. The other constituents are of no commercial importance. Eugenol may be obtained from clove oil by combining it with an alkali, removing the terpenes, setting free the eugenol and distilling. Its specific gravity increases on aging, owing to the formation of resinous or condensation products. Consequently, a perfectly pure material, when freshly distilled, will have a slightly lower specific gravity than required by the U S. Pharmacopœia. By treatment with alkalies, eugenol may be converted into iso-eugenol, which on oxidation yields vanilline.

Vanilline. Chemically, vanilline is the methyl ether of protocatechuic aldehyde and forms one of the main flavoring constituents present in vanilla beans. Vanilline alone, however, will not duplicate the entire flavor of vanilla, as it merely represents one of the constituents of the bean flavor. Vanilla beans contain in addition to vanilline, other substances to which the fine flavor of the beans is principally due. Popularly and quite erroneously, it has been thought that the resinous substances which are present contribute to the flavor. As a matter of fact, the resinous bodies in the bean when separated, tenaciously hold a small proportion of the active principles, but when perfectly pure, these resins have practically no odor or flavoring value. Synthetic materials are available, however, which duplicate the entire flavor of the finest beans and are free from resins or tannins which contaminate the natural bean flavor.

Allspice Oil (or Pimento). Another oil which contains a considerable proportion of eugenol (65 per cent) is the oil of allspice or pimento, official in the U. S. Pharmacopœia. It is used principally for flavoring. Most of the spices, herbs and other condiments utilized owe their flavoring value to essential oils.

Herb and Spice Oils. Among these, we may mention the oils of mace, nutmeg, caraway, celery, coriander, cumin, fennel, ginger, marjoram, parsley, sage, thyme and pepper, all of which are more or less complex in composition. Space does not allow their discussion in detail.

Cassia Oil. Another spice oil of importance is oil of cassia, improperly called in the U. S. Pharmacopœia, oil of cinnamon. Oil of cassia owes its main value to cinnamic aldehyde, which is present to the extent of about 80 per cent. This aldehyde is also produced by synthesis.

Ceylon cinnamon oil is worth about fifteen times as much as oil of cassia. It has a finer odor than cassia and while the content of cinnamic aldehyde is lower, ranging from 65 to 70 per cent, other constituents

are present which influence the odor considerably. For this reason, Chinese cassia oil and Ceylon cinnamon oil should not be confused or called by the same name.

Peppermint Oil. While speaking of the aromatic oils used as condiments or for flavoring, we must not overlook peppermint, which is produced so extensively in America. Oil of peppermint owes its chief value to menthol, an alcohol, having the formula $C_{10}H_{19}OH$, and some of the esters of menthol, principally menthol acetate. Japanese oil of peppermint is also marketed though often part of the menthol has been previously removed from it.

Eucalyptus Oils. In Australia, we find various members of the Eucalyptus family. They yield oils differing very much in chemical composition and odor and the exact species of tree from which the oil was obtained should always be mentioned. The ordinary commercial eucalyptus oil owes its medicinal effect principally to a body chemically known as eucalyptol or cineol. Eucalyptol is widely distributed throughout the essential oils in small proportion, but when present in large proportion as in eucalyptus oil, or when concentrated, it has a very disagreeable taste and odor. Consequently its use has decreased considerably in recent years, as other medicinal bodies have been found which are not as unpleasant.

Pelargonium or Geranium Oil. Oil of pelargonium is one of the more modern oils and is of considerable commercial importance, as it contains about 70 per cent of terpene alcohols, that is, both geraniol and citronellol, in varying proportions, according to the source. It shows that the same plant will yield other chemical substances when grown in different soils or climates. A number of varieties of pelargonium or geranium are distilled in Algeria and throughout northern Africa, as well as in some of the French islands, especially Réunion, and to a limited extent in southern France. The plant is common with us as a house plant and is known as "rose geranium." The oil is used in perfumery and soap making and also serves as the source of the valuable terpene alcohols, which may either be isolated and used as such or changed by synthesis into derivatives having a still higher perfume value.

Lavender Oil. Oil of lavender is distilled from a member of the mint family and while quantities are produced in England, the bulk of the product comes from southern France. French lavender oil is commonly valued by the ester content, estimating the mixture of esters as linalyl acetate. The so-called Mitcham or English lavender oil contains less ester but other constituents are present in small proportion which give a different perfume effect. The English oil commands a higher price. This is again an instance where the proportion of one constituent does not determine the value of a perfumery product. It is the quality of the constituents present that influences the value of the oil.

Linalool. Linalool is a terpene alcohol of high importance in the industry. It has the chemical formula $C_{10}H_{18}O$, and is widely distributed in nature. Mexican oil of linaloe is the principal commercial source of linalool, as this oil contains from 60 to 85 per cent. The oil itself has a crude odor, owing to impurities, but by proper physical and chemical methods the alcohol may be separated in very pure form. The so-called oil of female rosewood distilled in British Guiana contains a larger proportion of linalool and has a sweeter odor itself but the terpene alcohol separated from it, when properly purified, is in no way superior to the Mexican product, provided care has been taken to eliminate all impurities. Linalool also exists in several isomeric modifications differing somewhat in odor.

Neroli Oil. One of the oils which owes much of its odor value to esters of linalool, is the oil of neroli, distilled from orange blossoms in southern France. We have already mentioned methyl anthranilate and a number of other substances that contribute to the complex orange flower odor. Neroli oil, being made by steam distillation, of course does not represent the entire odor value of the flowers, but having become a commercial product many years ago, is esteemed by manufacturers of cologne and is also used as a flavor to a limited extent. "Orange flower water," so called, is obtained as a by-product in the process and contains the saponified portion of some of the constituents present in the blossom and may be had at a fair price, considering the fact that the purchaser must pay for the transportation of distilled water from Europe. A number of different varieties of neroli are known, neroli petale being the finest grade, neroli bigarade coming next in quality after which there are various inferior grades, ending with the so-called oil of petitgrain. This is imported from South America where it is distilled by crude native methods from twigs, leaves, unripe fruit, as well as flowers of the wild orange trees which have spread from those planted there when Spanish friars controlled that quarter of the world. Oil of petitgrain is a dangerous adulterant and is frequently used to dilute the more valuable neroli oils, both the natural and synthetic.

Rose Oil. We have already mentioned the history of oil of rose, usually known as Turkish otto. This continues to be one of the highly prized perfumery products used throughout the world. Turkey does not produce even a small proportion of the crop, almost all of it comes from Bulgaria. Yet it must be remembered and repeated that distilled oil of rose has only part of the perfume of the flower. The very act of steam distillation destroys some of the most valuable constituents present in the petals. As previously mentioned the oil consists largely of geraniol, citronellol, and allied compounds with a small proportion of their esters, as well as about 20 per cent of an entirely odorless waxy hydrocarbon belonging to the paraffine series. Much of the oil is impure. The official figures show the importation into Bulgaria of

quantities of products that may be used as adulterants for oil of rose and the export of a great deal more rose oil than the statistics show has been produced.

There are many varieties of roses but only two of these are commercially cultivated. Some of the other varieties have a very sweet odor but are not grown for perfumery purposes. Many other constituents are present in these members of the rose family. In order to produce their odors we have to utilize a number of different chemical compounds.

Patchouly Oil. Oil of patchouly is an illustration. When added to rose products in infinitesimal proportion, it helps to duplicate the peculiar odor of the white rose. The patchouly plant is principally obtained from the Straits Settlements and Java, where it has been cultivated so long that it has almost wholly lost the habit of flowering. The oil, which is distilled from the leaves, increases in value on aging. By chemical methods, the oil may be purified and the undesirable constituents which have a moldy, disagreeable odor, removed. The resulting products can be used without hesitation in the finest perfume combinations, but only in small proportion as the strength is enormous. If employed in too large a quantity the effect will not be agreeable.

Sandalwood Oil. While considering East Indian oils, we must not overlook oil of sandalwood, which has been known for many years and has always been highly esteemed in the Orient. Sandalwood itself is an ancient constituent of incense and the trade in this rare wood is so valuable that it has been monopolized by the government, auction sales being held at regular periods under supervision of East Indian officers. But little of the wood is distilled in the Indies, the greater part is exported to Europe and America where the oil is produced by modern methods. The principal portion of the oil is known as santalol, a rather complex chemical substance which is both alcoholic and aldehydic in nature and consists of a number of distinct chemical individuals. Santalol is much more valuable to the perfumer than sandalwood oil because it represents only the useful portion of the oil, as the ill-smelling constituents have been removed. From some of the fractions of sandalwood oil, the writer succeeded in isolating portions which have odors almost identical with certain fractions obtained from oil of patchouly, showing that these oils, produced in the same climate by a tree and herb which have no botanical relation, contain similar compounds.

Cedar Oil. The cedar-like odor of oil of sandalwood has often led to its adulteration with oil of cedar, which is much cheaper and may be had in unlimited quantities. Much cedarwood oil is distilled from the sawdust or shavings produced in manufacturing lead pencils. A finer grade finds a limited market, being used in microscopical work.

Juniper Oil. Cedar is a member of the Juniper family. Juniper berries and their oil have long been used for making gin and for flavoring. The berries have also a historical interest since in some sections of Central Europe,

the custom prevails, when a death occurs in a house, of roasting the berries in a red-hot pan, so as to have the odor diffused throughout the rooms. Apparently this is a tradition which has been handed down from pagan times, since juniper berries formed part of the sacrificial offerings of the early Teutons.

Turpentine Oil. Juniper oil contains a considerable proportion of terpene and this brings us to the field of turpentine and allied products. Turpentine is a widely used solvent and is becoming scarcer each year, so that lately even the old stumps have been utilized to produce a cheap grade. While not a perfume material, the oil is certainly an essential oil and it also serves as a source for some constituents of our most valued flower odors. Turpentine may be hydrated, forming terpene hydrate, which in turn, by treatment with acids, may be converted into terpineol. This is a terpene alcohol which exists in many of the finest flower oils, though in numerous modifications, widely varying in physical properties, optical rotation, boiling-point and melting-point and differing just as widely in odor. The common terpineol much used as a soap scent, is a syrupy oil looking like glycerin and is not adapted to finer perfumery. Purified products, however, are also marketed and are invaluable. (Muquet, Muquet Ideal, etc.) Isomeric modifications of terpineol are present in lilac, tuberose, mimosa, ylang ylang, lily of the valley, and many other exquisite flower oils.

Ylang Ylang Oil. Ylang ylang oil has long been one of the most valuable products of the Philippines. The distilled oil is a very complex body which differs considerably from year to year and according to the method of production. In fact, ylang and cananga, a cheaper oil, are derived from the same tree. The best ylang ylang oil consists of the first portion of the steam distillate. It contains a larger proportion of esters. Many of the chemical bodies that we have described are present in this oil, therefore it is a fine example of a complex natural product. It contains benzyl alcohol, benzyl acetate, benzyl benzoate, benzyl salicylate, methyl anthranilate, methyl benzoate, methyl salicylate, geraniol, geraniol acetate, linalool, linalyl acetate, eugenol, iso-eugenol, methyl eugenol, methyl iso-eugenol. This list while long is by no means complete, as a number of allied bodies, especially other esters, are also present. Even all these together will not give the right odor, until the characteristic constituent is added which converts the product into ylang ylang. This body is the methyl ether of para-cresol, which is enormously powerful and therefore must be used with great care. Traces of para-cresol itself and of guaiacol ethers are also present in the oil.

Much as science has advanced in the last few decades we must appreciate that organic chemistry is still in its beginning. We have learned a great deal. We have found, isolated, and reproduced many of the constituents present in plants, but like the students of biology, before powerful microscopes became available, we wander among undreamed of

wonders. Let all students interested in industrial chemistry remember that every successful advance of the future must be founded on Science. Let us all assist in building the structure, willingly giving our best toward the ultimate success, even if our individual efforts may be forgotten in years to come.

XXX

RESINS, OLEO-RESINS, GUM-RESINS, AND GUMS

ALLEN ROGERS

Source. These products are all derived from exudations of plants and as a rule are oxygenated bodies. When mixed with certain percentages of the natural essential oil accompanying them, they are known as oleo-resins or balsams. If mixed with mucilaginous matter they are harder and known as gum-resins. Gums are amorphous bodies which are either soluble in or gelatinize with water, but are insoluble in alcohol. True resins are distinguished from gums in that they are all insoluble in water, free from odor or taste, form compact masses, and are usually of an aldehydic or acid nature. Fossil resins are found in the earth, usually in the form of irregular lumps, and often contain perfect specimens of fossil insects and leaves.

Amber. Amber is a fossil resin occurring as small masses in alluvial deposits in various parts of the world. According to Goefert it represents the resinous exudation from about fifty different kinds of coniferous trees. It is found chiefly in Prussia along the shores of the Baltic where it is thrown up by storms, or in some localities is even mined. Large deposits also occur in some of the lakes on the eastern coast of Courland. Small deposits have been found in New Jersey and Maryland, but not of sufficient magnitude to be of commercial importance. The largest single mass of amber ever reported weighed thirteen pounds. It is usually associated with lignite and often contains the fossil remains of insects and vegetation.

Amber is a brittle solid, permanent in the air, and is susceptible to a very high polish. By application of friction it becomes negatively electrified. Its color is usually from light to deep brownish yellow, although it sometimes possesses a reddish brown or bluish color. It is tasteless and odorless when cold, but gives off a peculiar aromatic odor when heated. It is generally translucent, though sometimes transparent or opaque. It is scarcely acted upon by water or alcohol. When heated in the air, it softens and finally melts at 286° C., which property makes it of value in the manufacture of varnish. When subjected to distillation several products result among them being succinic acid, esters, and oil of amber. Amber is used in making high grade varnish

and finds extensive application in the manufacture of tobacco pipe stems and articles used for ornamental purposes.

Animé. The substance known as *gum animé* is a resin supposed to be derived from the *Hymenœa courbaril*, a leguminous tree of South America. The resin exudes from wounds in the bark and is also found under ground between the principal roots. It occurs in small irregular pieces of a pale yellow color, sometimes being of a reddish cast. It softens in the mouth, and when in a powdery condition adheres to the fingers. It readily melts on being heated giving off an agreeable odor. It consists of two resins, one being soluble in cold alcohol and the other insoluble, and a small amount of volatile oil. Animé was formerly used to quite an extent in the preparation of ointments and plasters; but at present is only employed as incense or in the manufacture of varnish.

Burgundy Pitch. When incisions are made in the Norway Spruce a sap exudes which is collected in small troughs, or holes dug at the foot of the tree. It is purified by filtering through straw and allowed to harden, subsequently being boiled with water to remove the volatile oil.

Colophony or Common Rosin. This product is obtained in the preparation of oil of turpentine from crude turpentine. The latter is an oleo-resin obtained as an induced exudation from the pine tree. The sticky viscid liquid or crude turpentine, is subjected to steam distillation whereby about 17 per cent of the volatile oil of turpentine passes over, leaving a resinous matter, or rosin, in the still. Many grades of rosin are found in the market, being distinguished by letters (W.W.—water white) to designate their purity. It is also quoted as *virgin*, *yellow dip*, and *hard*. In its purest state rosin is beautifully clear, possessing a yellow color with an olive tinge. This is obtained from the first runnings after the tree is "*boxed*." The greater part of the rosin, however, comes under the head of yellow dip, which is obtained by distillation of crude turpentine. The hard rosin is very dark in color and is obtained from the scrapings after the juice has become too thick to run into the box.

Rosin is heavier than water, having a specific gravity of 1.070 to 1.080; it is easily fusible, becoming soft at 100° C., melts to a liquid at 152.5° C., gives off bubbles of gas at 157.5° C., and is decomposed at red heat. It is soluble in alcohol, ether, benzol, carbon disulphide, acetic acid, fixed or volatile oils, and in solutions of potassium or sodium hydroxide. When distilled in vacuo, rosin undergoes very little decomposition; but if heated in a retort it yields gaseous, liquid and solid decomposition products. That portion of the liquid distillate boiling below 360° C. is known as *rosin spirits;* resembling turpentine very closely for which it is largely used as a substitute. The portion distilling above 360° C., known as *rosin oil*, is much heavier and darker than rosin spirit and must be purified before use. This purification is accomplished by treatment with sulphuric acid, followed by lime water and then distillation.

Copal. This is a resinous substance derived from the exudation of several varieties of trees indigenous to the East Indies and South America, as well as parts of Africa, the Philippine Islands and other places. The gum is sometimes taken directly from deposits on the tree or is found imbedded in the earth. That variety of copal known in commerce as *gum Zanzibar* is found usually under the ground. Another variety with indented goose-flesh surface, known in the English market as animé, is dug from the earth.

Copal varies in appearance and properties depending upon the source from which it is derived. It appears in roundish, irregular, or flattish pieces, often with a rough indented surface due to sand impressions while it was in a soft condition. In color it ranges from colorless to yellowish brown; it is more or less transparent, very hard, odorless, tasteless, and has a specific gravity of from 1.045 to 1.130. It is insoluble in alcohol, partly soluble in ether, and slightly soluble in oil of turpentine. When heated it melts, giving off gases to the amount of 15 to 20 per cent of its weight. Its properties are changed by this treatment so that it becomes more soluble in alcohol, ether, and oil of turpentine; which characteristic renders it, like other resins, suitable for the preparation of varnish.

Dammar. This is a resin which exudes in drops from a coniferous tree, *Agathis loranthifolia*, and is collected after it dries. It is soluble in essential oils, in benzol, and to a slight degree in alcohol and ether. Owing to its light color and ready solubility in turpentine it finds extensive application in the manufacture of light-colored transparent varnishes.

Dragon's Blood. This is a resinous substance obtained from the fruit of several species of small palms growing in Siam, the Molucca Islands, and other parts of the East Indies. An exudation appears on the surface of the ripe fruit, which is separated by rubbing, by shaking in a bag, by exposing to steam, or by decoction. The finest product results from the first two methods. It comes on the market in two forms: either as small oval drops (*tear dragon's blood*) covered with the leaves of the plant and connected in a row like beads; or in cylindrical sticks eighteen inches long and about half an inch in diameter, covered with palm leaves and bound with slender strips of cane. An inferior product, prepared by boiling, the fruit in water, is in the form of flat circular cakes (*cake dragon's blood*).

Dragon's blood is odorless, tasteless, insoluble in water, but soluble in alcohol and ether, also soluble in the volatile and fixed oils, forming red solutions. Its principal use is in the coloring of varnish.

Elemi. This resin is obtained by making incisions into the trees, through which the juice flows and concentrates on the bark. Elemi comes on the market either as soft (Manila elemi) or hard (Brazilian elemi) being of various colors from light yellow to greenish white. It

is soluble in alcohol and other solvents, its chief use being to impart toughness to varnishes made from harder resins.

Guaiacum. This resin is the concrete juice of the tree *Guaiacum sanctum*, obtained by several different methods. The simplest method is that of spontaneous exudation, or by making incisions in the trunk. Another method is to saw the wood into blocks boring holes in them longitudinally, placing one end of the block in the fire and collecting the melted resin which flows out at the opposite end. The plan most commonly used, however, is to boil the chips and sawdust with a solution of common salt, and skim off the substance which rises to the surface. Guaiac appears in the market as irregular lumps often mixed with small fragments of bark and sand. The purest form comes in small lumps, "*tears*," which result from natural or induced exudation.

Kauri. This is an amber-like resin, varying from light cream to brownish yellow in color. It is the result of exudation from the tree *Agathis australis*, and is dug in large quantities from the ground in New Zealand. It is used very extensively in varnish making and like copal must be first heated or "*run*" before it becomes soluble in oils.

Lac. This is a resinous substance obtained from several varieties of trees growing in the East Indies, especially from *Croton laccifera*. The lac is found in the form of a crust surrounding the twigs and is supposed to be an exudation from the bark caused by the sting of an insect, *coccus lacca*. Some authorities believe that the exudation comes from the bodies of the insects themselves, which become imbedded in great numbers in the concreted juice, through which the young eat their passage and escape. Among the several varieties of lac met with in commerce are *stick-lac*, *seed-lac*, and *shellac*.

Stick-lac. This is the resin as it is taken from the tree with the encrusted resin surrounding the twigs. It is of a deep reddish brown color, odorless, and possessing a bitter taste. The surface is perforated with a large number of minute holes, which, when broken, exhibit oblong cells often holding a dead insect. When placed in the mouth it colors the saliva a beautiful red and imparts the same color to warm water.

Seed-lac. This consists of small irregular fragments which have been broken from the twigs and partially washed with water. It varies in color from light to dark brown, is odorless, almost tasteless, and imparts only a slight color to the saliva.

Shellac. This is the form of lac with which we are the most familiar and results from the melting of stick-lac or seed-lac, which has previously been washed free from its soluble coloring matter, and pouring it on a smooth flat surface to harden. A description of the native operation as given by Valentine Ball [1] is quoted below:

"The stick-lac is first placed between two powerful rollers, which, by a simple arrangement, admit of any degree of approximation. The lac

[1] "Jungle Life in India," N. R., June, 1880.

is thus crushed and separated from the woody portion by screening; it is next placed in large tubs half full of water and is washed by the coolies, male or female, who, standing in the tub, and holding to a bar above with their hands, stamp and pivot about on their heels and toes until, after a succession of changes, the resulting liquor comes off clear." The disposal of the liquor drawn off at the successive washings will be spoken of farther on. "The lac, having been dried, is placed in long cylindrical bags of cotton cloth of medium texture and about ten feet long by two inches in diameter. These bags when filled have the appearance of enormous bologna sausages. They are taken to an apartment where there are a number of charcoal furnaces. Before each of these are one principal operator and two assistants. The former grasps one end of the long sausage in his left hand and slowly revolves it in front of the fire and at the same time one of the assistants twists in the opposite direction. The roasting before the glowing charcoal soon melts the lac, and the twisting of the cloth causes it to drop into a trough formed of the leaves of the American aloe. When a sufficient quantity in a molten condition is ready in the trough, the operator takes it up in a wooden spoon and places it in a wooden cylinder some eight or ten inches in diameter, the upper half of which is covered with sheet brass. The stand which supports the cylinder gives it a sloping direction away from the operator. The other assistant by means of a strip of aloe, with a rapid and dexterous motion, spreads out the lac into a sheet of uniform thickness which covers the upper portion of the cylinder. The operator now cuts off the upper edge with a pair of scissors and waves it about in the air till it becomes crisp." The sheets made in this manner break easily and thus form little flakes or *shells* which gives the name shellac.

"The dark red liquor resulting from the washing above described is strained to remove foreign matter. It is then passed into vats and the suspended matter is allowed to settle out, which is then washed, pressed, and comes on the market as *Lac-dye*."

Lac is partly soluble in alcohol, forming a cloudy liquid, largely used as a varnish under the name shellac varnish. Lac is also soluble in alkaline and borax solutions in which condition it is employed as a stiffening for hats, in the finishing of leather, and for other purposes. Shellac is readily bleached by treatment with alkaline hypochlorites or by treating the alkaline solution with chlorine gas. The lac is precipitated by neutralizing the alkali and is then melted in hot water and "*pulled*" which makes it appear whiter and easier to handle.

Mastic. This is a resinous exudation from the *Pistacia lentiscus*, a tree cultivated in the Grecian Archipelago. Incisions are made in the trunk and large branches, from which the juice on exuding either hardens on the bark in tears or drops to the ground, where it is caught on cloths. It is of a light yellow color and nearly odorless. It is soluble in alcohol

up to about 90 per cent, and is used to quite an extent in the preparation of spirit varnish.

Sandarac. This resin resembles mastic very closely and comes on the market in the form of tears. It is more soluble in alcohol, however, and is employed largely in the preparation of transparent varnish.

Oleo-Resins. The most important members of this class of compounds are *Benzoin*, *Peru*, *Tolu*, and *Storax*. They are all mixtures of resins with essential oils, and consequently have a much softer consistency than the resins. They are used especially in pharmacy and having practically no industrial application will not be considered in detail in this chapter.

Gum-Resins. The more important members of this class are *Ammoniacum*, *Asafoetida*, *Euphorbium*, *Galbanum*, *Gamboge*, and *Myrrh*. They are mixtures of gums and resins, form emulsions with water and are all largely used in pharmacy, gamboge being also employed as an orange red pigment.

Acacia. Both *Gum Arabic* and *Gum Senegal* are included under this head, as they are derived from plants of the acacia family usually found in Africa. It forms lumps of various size with color ranging from white to reddish brown. It is soluble in both cold and hot water and is used in the preparation of emulsions, in thickening ink, in water colors, textile printing, sizing cloth, and in the preparation of mucilage.

Agar-Agar. This is also known as *Bengal isinglass* and *Japan isinglass*. It is derived from certain algae from which it is obtained by boiling in water. It comes on the market as long white masses. It is used as a sizing for cloth and as a culture medium for bacteria.

Iceland Moss and Irish Moss. These are derived from a form of sea weed which on boiling with water produces a jelly much used in the textile and leather industries as well as for edible purposes.

Tragacanth. This is a gummy exudation from *Astragalus gummifer*. It is odorless, nearly tasteless, and of a very light yellowish to white color. It usually comes into the trade in a flaky condition. Placed in water it absorbs a certain amount and swells up very much, forming a soft adhesive paste. If the paste is agitated with more water, it forms a uniform mixture, which, however, will settle out on standing as only part of the gum goes into solution. It is largely used in calico printing and for other purposes where an adhesive is required.

Caoutchouc or India Rubber. India rubber is the coagulated product obtained from the milky juice of a large number of trees, creepers, and shrubs, native of nearly all tropical countries; although the finest grades (Para rubber) come from South America. The juice is collected during the months of July, August, October, and November. It is coagulated by exposure in thin layers to the smoke of burning palm nuts; or it is boiled with water, or with dilute acid, salt water, or lye; alum is sometimes added when the product becomes wet and porous.

Purification. As rubber comes on the market it is very impure, containing water, sand, fibers, wood, and various other materials. These impurities are removed by a washing process which is carried out in strong machines built for the purpose, consisting of corrugated rollers, which flatten the lumps into thin sheets thus aiding in the washing process. The sheet rubber thus obtained is dried very thoroughly by hanging in a warm room for several weeks. Good Para rubber loses about 15 per cent of its weight by this washing process, while some inferior grades sustain a loss as high as 40 per cent.

Properties of Rubber. India rubber, in its highest state of purity, is practically colorless, but darkens on exposure to air and light. The commercial product, however, is nearly black, due to discoloration by smoke produced during the process of coagulation. It is insoluble in water, but absorbs about 25 per cent on prolonged immersion. It is sticky so that its freshly cut surfaces will unite again very firmly. Dilute acids and alkalies are without action upon it, but strong acids and chlorine rapidly destroy it. Rubber is a very elastic substance at ordinary temperatures, but if heated it becomes sticky and loses its elasticity at about 120° C., finally melting at 150° C. It is very soluble in carbon disulphide and chloroform, and to a limited extent in ether, oil of turpentine, benzol, and naphtha.

Compounding. For manufacturing purposes the crude washed rubber is mixed with various materials. The operation is carried out in a mixing mill, which consists of a pair of smooth, hollow iron rollers, one of which is heated by steam to a temperature of about 80° C. The materials which are to be incorporated may be vulcanizing agents, coloring matter, fillers, inerts, weighting materials, rubber substitutes, or cheap gums. The mixing and grinding are here carried on until a homogeneous mass is obtained, which can then be worked into any form desired. As unvulcanized rubber is very sticky it is necessary to dust the fresh surfaces with talc or starch to prevent adhesion.

Vulcanization. As natural rubber is greatly affected by change of temperature it is impossible to use it for many purposes, but owing to the discovery of vulcanization these difficulties are obviated and we have a product which is of the greatest value to mankind. This process is brought about by means of the chemical change produced when the rubber is heated with sulphur, metallic sulphides, and metallic oxides. The process most generally employed is to incorporate from 7 to 10 per cent of sulphur with the masticated rubber, using every precaution to see that the ingredients form a homogeneous mass. It is in this condition that the mixture is *wrought* into sheets, tubes, shoes, or other desired shape ready for the heat treatment. The goods are next put into a hermetically sealed boiler where the steam is injected under a pressure of from 50 to 60 lbs.; three to four hours being necessary for the complete vulcanization. When it is desired to retain the brilliancy

of the product, stoves, which are heated to a temperature of 130–150° C. are used in place of the boilers. Whether stoves or boilers are employed, the same chemical action takes place and the sulphur is uniformly distributed throughout the mass.

Parks' Process. This process, discovered by Alexander Parks (British patent 11,147; 1846), consists in treating the rubber with sulphur monochloride in the cold and is very widely used, especially for vulcanizing small thin articles. The objects to be vulcanized are immersed from one-half to three minutes in a solution consisting of 2½ lbs. of sulphur monochloride dissolved in 100 lbs. of carbon disulphide. On removal from the bath the goods are dried at a temperature of about 25° C. (77° F.), again immersed for one minute, washed with dilute sodium carbonate, then with water, and finally dried. With slight changes only, the method is still being used as indicated in the original patent. Vulcanization destroys the adhesive property of rubber, but renders it much more elastic.

Loading. Many substances such as barytes, litharge, clay, chalk, and other materials are sometimes added to rubber during the mixing process which act as fillers. These materials, however, are only used on inferior grades.

Rubber Substitutes. The increasing demand and high price of rubber has stimulated many investigators to try to find some natural or artificial product having analogous properties. The result of this work has been that we now find a large number of rubber substitutes on the market. Claims have also recently been made that it is possible to make true synthetic rubber. The most common rubber substitutes are made by acting upon linseed or some other vegetable oils with sulphur monochloride. The proportion of 100 parts of oil to 25 of chloride gives the hardest product, while less amounts of sulphur monochloride give a softer material. These sulphurized oils are usually mixed with low-grade rubber and coal tar or resins; being sometimes employed even without any rubber.

Reclaimed Rubber. In the manufacture of rubber goods it is very essential that some means should be provided to use up the waste material such as scraps, condemned or defective articles, as well as rubber which has become unfit for further use. Among the oldest and most widely employed method is that of Goodyear's, which consists in reducing the waste to a finely divided state, mixing with normal rubber and sulphur, and heating for several hours under heavy pressure. The reclaimed rubber has very little strength and is used only in connection with fresh gum.

Application of Rubber. Rubber is a substance which finds a very extensive application. Among the most common uses may be mentioned: Rubber shoes, rubber boots, overshoes, rubber coats, rubber hats, bicycle, carriage, and automobile tires, hose, cements, varnishes,

tubing, bottles, brush handles, combs, ebonite, and a score of other uses.

Gutta-percha. This product is obtained from the latex of the tree *Dichopsis gutta* which grows native in the East Indies. It is isolated by grinding the bark and leaves by which method the little sacs are ruptured. The grinding takes place under water so that the chips and sand may be readily removed. The plastic mass of gutta percha collects in the vessel and on removing may be rolled out into sheets. For many purposes gutta percha is used alone, while in other cases it is mixed with rubber.

XXXI

VARNISH

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Definition. Varnish is a liquid, designed to form films to cover surfaces, which on exposure to the air hardens and forms a more or less transparent and glossy coating which improves or better displays the surface to which it is attached and to some degree protects it from dirt and injury.

Classes of Varnish. Varnishes may be divided into two classes: those which harden by evaporation of the solvent; such are spirit-varnishes; and those which absorb oxygen from the air and by chemical changes are made into hard films; these are oleo-resinous varnishes, and constitute the largest, most important and varied kind, used for a great variety of purposes.

Spirit Varnish. Spirit varnishes consist of suitable solids, dissolved in volatile solvents; the most important is shellac, which may be regarded as typical. It consists of shellac resin dissolved in alcohol, and when spread out in a film the alcohol evaporates, leaving the resin as a thin layer over the surface to which the varnish has been applied. It will be evident that the alcohol has served practically as a mechanical means of spreading the resin in a thin and uniform film; its cost is to be added to that of the labor, and the use and wear of utensils, required in applying the varnish, as all that we have at the end of the work is the film of resin.

Shellac Varnish. Gum-shellac, as the shellac resin is called, is usually in thin elastic flakes of a yellow or reddish or brownish-yellow color. Put a gallon of alcohol in a clean earthenware jar of two gallons capacity; at the close of the day's work gently drop into this three or three and a half pounds of flake shellac, without the slightest avoidable agitation; cover and let stand until the next day. Then with a clean wooden rod stir it for a few minutes, and during the day stir it for a minute at a time once an hour or so, and before night it will be dissolved. That is, the resin will be dissolved; but shellac naturally contains a little wax (4 per cent) which is insoluble and makes the solution milky

or muddy and opaque; the film is, however, transparent. Shellac may be bleached by dissolving it in an alkaline aqueous solvent and then treating it with chlorine; the shellac precipitates when the alkalinity is removed, and is white. This is dried and looks much like pieces of white candy; it cannot be dissolved in the manner described, as it is in lumps and sinks to the bottom; it is therefore dissolved by agitation, usually in a revolving barrel or churn; this is indeed the way orange shellac is made on a large scale. The latter is soluble in 85 per cent alcohol, though it is more satisfactory to use stronger; but white shellac already contains some water and requires 95 per cent alcohol.

Insoluble Shellac. White shellac is liable to pass into a modified form insoluble in alcohol; this especially is likely to occur if heated above ordinary temperatures or if kept in a dry place too long. For some purposes it is desirable to get rid of the five to ten per cent of water in white shellac before dissolving it; it is spread on trays in a drying room, but not heated very much; it is better to use artificially dried air at ordinary temperatures; in any case it must be dissolved as soon as possible.

Shellac varnish dries by the evaporation of the solvent, and appears to dry almost immediately; but some of the liquid is retained for a time, and it is not practicable to apply many coats in rapid succession, or it will be found that the whole has a waxy character, persistent and troublesome. Varnish made with "denaturized" alcohol is especially slow to dry; commercial wood alcohol is much better.

Damar Varnish. Alcohol is not the only solvent used in making spirit varnishes. Damar varnish is damar resin dissolved in spirit of turpentine, and dries by the evaporation of the latter. Both this and shellac are often adulterated with common rosin, or colophony. Damar may be dissolved cold, in a churn; some pulverize it before dissolving; or make it with the aid of heat, preferably in a steam-heated vessel. The varnish is a milky liquid, but may be cleared by filtration or otherwise. If made hot it can be cleared more easily. Five or six pounds of resin are dissolved in one gallon ($7\frac{1}{2}$ lbs.) of spirit of turpentine. The film is transparent and practically colorless.

Mastic and Sandarac Varnish. Sandarac is another resin usually dissolved in spirit of turpentine; another is mastic; both are also mostly soluble in alcohol. Amyl and methyl alcohols are for some resins better solvents than ethyl alcohol; and acetone added to alcohol greatly increases its solvent power.

Petroleum benzine is very commonly added to turpentine to cheapen it; it has the advantage of evaporating more readily and perfectly, and some of the heavier grades are for many purposes equal and perhaps superior to turpentine.

Pyroxylin Varnishes. Pyroxylin varnishes are a variety of spirit varnishes. The solid part is cellulose rendered soluble by acting on

it with nitric acid, making cellulose nitrates of various compositions. The principal solvent is amyl acetate, which may be extended or diluted with various liquids, as benzole, which have no real solvent action on the pyroxylin, but do not inhibit the solvent action of the amyl acetate; differing in this respect from the action of water on alcohol. Pyroxylin films are somewhat hard and stiff, and may be made more flexible by adding a fixed oil, as castor, cotton, or linseed, to the solution.

Lacquer. Spirit varnishes are often called lacquers, and are sometimes colored by aniline or other dyestuffs. Both asphaltum and coal-tar pitch are soluble in turpentine and benzine, or coal-tar naphtha, and are used as spirit varnishes; but more often with the addition of oil. Rosin is almost always added to asphaltum, but not necessarily.

Oleoresinous Varnishes. The greater part of the varnish made is compounded of oil, resin, and spirit of turpentine, and is of great variety of composition and uses. Almost all the oil used is linseed. A little tung, or Chinese wood oil is used, but inconsiderable in amount as compared with linseed. This oil is usually subjected to some preliminary treatment; it is, as purchased from the makers, well settled and filtered, and free from cloudiness; it may be remarked that a mere trace of water causes a cloud, and the not uncommon belief that oil must be freed, by some treatment, from water and "mucilage" is a mistake, as oil of ordinary good quality is quite free from such things.

Breaking. Freshly-made oil, if heated to 400° F., suffers a slight partial decomposition; gelatinous clots appear in it, and it is said to "break"; this is due to the phosphates it contains, and any treatment which will destroy these will prevent its "breaking." A common way is to add, with agitation, a little sulphuric acid; the oil is afterward washed with water, and is found to be bleached somewhat; it may be bleached more by agitating warm, with fuller's earth, and filtering; but not all the color can be removed by any known means. What is known as "varnish oil" has been treated in some way so that it does not break; and if such oil is heated quickly to about 500° F. and cooled, it is found to be considerably bleached. This is a common practice. Sometimes a very little of some lead or manganese compounds are added before doing this. It is usually put through some such treatment and allowed to settle for a month or more before being used in varnish.

Weight of Oil. A gallon of linseed oil weighs 7.75 lbs.; but in selling oil by the barrel or larger quantities it is a commercial practice to call 7.5 lbs. a gallon, so that in buying it one gets about 3 per cent less in fact than the nominal amount. No charge, however, is made for the barrel —an oil-barrel is usually a 50-gal. cask—the value of which is usually more than the 1½ gallons lacking. In making paint or varnish the full weight or measured gallon is always the unit.

Resins. Asphaltum is a mineral, but practically all the resins used in varnish are of vegetable origin, and most of them from tropical or

sub-tropical countries. They exude from trees, where the bark is injured, and form lumps varying in size from very small pieces up to masses of many pounds weight. In a few cases resin which is collected from living trees is used; but for the most part the varnish resins are dug up from the ground, the trees having fallen and decayed, and the lumps of resin having become buried, sometimes as much as six feet below the surface. Having for many years been thus buried they have undergone change, become harder and better suited for use. After being dug up, cleaned, and sorted, the resin is packed in boxes or bags, and in this condition market resins are bought at prices ranging from about 75 cents per pound for the choicest sorts to as little as 5 cents per pound for some inferior kinds. Probably a fair average price (1911) would be about 30 cents. The valuable qualities are clearness, hardness, high melting point, pale color, luster, and perfect solubility, after melting, in oil. As a rule these resins are not soluble in oil or in spirit of turpentine or benzine; but after melting they are found to be so changed that they dissolve in hot oil.

Melting Resins. Most of them require a temperature of 550 to 650° F. to melt them properly, and in melting they lose 10 to 25 per cent of their weight; some species lose more and some less; the best and hardest resins lose about 25 per cent. If this is done in the laboratory with proper precautions it will be found that the temperature of the melted mass is much higher than that of the vapor, showing that chemical decomposition has occurred. All light-colored resins darken on melting, some more than others. The greater part of the distillate can be condensed to a liquid; this is not done in this country, but in England and Europe it is common, partly because by refining the liquid may be made use of as a turpentine substitute, and partly because it prevents the escape of gases which may be thought objectionable in residence sections of cities.

Copal. Copal is a popular or trivial name applied to varnish resins, about as indefinite in its meaning as the term "metal." It was originally a Central American native word, and was applied to any resin. It is now used only for varnish resins, but does not designate any particular substance. In the varnish factory resins are commonly called "gums," although true gums, such as gum-arabic, are water-soluble. Colophony is always, and correctly, called rosin, and is never spoken of as a gum. Gum-varnishes mean oleo-resinous varnishes free from rosin.

Varnish Nomenclature. One hundred pounds of resin is the conventional unit, and varnishes are described as containing so many gallons of oil to this 100 lbs. of resin, weighed before melting. Thus a 20-gal. Kauri, or 20 K, is a varnish made from 100 lbs. Kauri resin, 20 gals. linseed oil, and (probably) 30 gals. spirit of turpentine, the amount of the latter not being mentioned. The grade of resin may also be mentioned; thus, "20 Brown 3 half benzine" would be 100 lbs. Kauri of the grade

known as No. 3 Brown Kauri, 20 gals. oil, 15 gals. spirit of turpentine (turps for short), and 15 gals. benzine. This is a fairly accurate description and any varnish-maker would recognize it. 100 lbs. of any resin counts for about 6 or 6½ gals. in the batch; turps weighs 7.2 lbs. and benzine a little more than six lbs. per gal. So this would figure as follows:

100 lbs. resin	= 75 lbs.	= 6 gals.
20 gals. oil	= 154 lbs.	= 20 gals.
15 gals. turps	= 108 lbs.	= 15 gals.
15 gals. benzine	= 90 lbs.	= 15 gals.
	427 lbs.	= 56 gals.

Actually it will be more like 420 lbs. = 55 gals., because at least a gallon of the thinner will be lost by evaporation.

Linoxyn. When linseed oil is exposed to the air, either by blowing air through it or by exposure in thin films, it is changed into an elastic substance, not sticky or greasy to the touch., called linoxyn. This is an oxidation product, and weighs considerably more than the original oil, probably about one-fifth more; different experimenters have reached various results. Its specific gravity is higher than that of the oil; and it is apparent that the latter has contracted in volume as well as increased in weight. This product is insoluble in oil and in turpentine and most of the other oil-solvents, and is the elastic ingredient of oil-paints and oleo-resinous varnishes. When oil is spread out in a film and exposed to the air it does not for some time appear to change, but after a certain time it rather suddenly changes into a semi-solid, gelatinous, sticky condition; up to this point, being a liquid, any contraction which may have occurred causes no notable change; but now a somewhat solid film quickly forms, in which contraction produces a state of tension. It is obvious that if this film is at all inclined to be porous, contraction will open the pores, because it stretches the solid part of the film away from the openings; and this is probably the cause of the porosity of dry linoxyn films.

Porosity. If, therefore, we can add something to the oil which will act as a flux, and postpone this preliminary setting until the compound, by absorbing more oxygen, is in a more stable condition, we shall decrease the final porosity of the film. This is probably what we do when we dissolve a resin in the oil. The resulting compound—varnish—does not take its initial set until it is more completely oxidized, and the film thus formed is more nearly free from pores than a pure linoxyn film.

Varnish Films. Such a film has two other advantages. First, it is harder, and resists abrasion better, and it is smoother, which has the same effect; second, as the liquid varnish is more viscous than oil, it may be applied in a somewhat thicker layer, and a thick film is more

lasting than a thinner one. The most obvious quality of a varnished surface is its smoothness and lustrous appearance; its brilliancy depends not only on its smoothness but also on its high refractive power as regards light; those varnishes having the highest refractive indices being the most brilliant. This is increased, in general, by increasing the proportion of resin.

Outfit for Making Varnish. The varnisher-maker's outfit is very simple. A varnish kettle is a cylindrical copper vessel, about 36 ins. in height and from 30 to 36 ins. in diameter, with a flat bottom. It has a loose cover, which is provided, in the middle, with an upright cylindrical outlet or "chimney" about 5 ins. in diameter and 8 ins. high; it has also a hole in it for a stirring-rod; and some styles have an opening for a large funnel. The kettle is loosely set on an iron truck or wagon, with three or four wheels, so built that the bottom of the kettle, which rests on a ring only slightly less in diameter than itself, is not more than a couple of inches above the floor. There is a fireplace, consisting of a round pit sunk below the floor level, lined with fire-brick and having a grate, under which is an ash-pit and suitable air-flue, and nearly over which, a little in the rear, is a spacious chimney which carries off the products of combustion and also the vapor from the kettle. The fuel is coke, which burns freely and without much flame, which might set fire to the kettle vapor. The stirring-rod is of stiff steel, 5 or 6 ft. long, with a wooden handle. There is a large funnel, for use in pouring in oil, which may be put into the chimney in middle of the cover, or into a special opening in the cover near one side.

Varnish Making. Into this kettle is put 100 or more commonly 125 lbs. of resin, the kettle is placed on the wagon, and wheeled over the hot fire. As the resin melts, the escaping gases cause foam, which makes it necessary that the kettle should be of considerable height and capacity. In about half an hour all the resin is melted; some varnish-makers melt with the thermometer in the melting resin, others depend on feeling the disappearance of lumps with the stirring-rod; and from time to time the latter may be withdrawn and the adhering resin examined. Without removing the cover, the oil, which has previously been heated in another receptacle, is added; some previously draw the kettle from the fire, others add the oil when the kettle is still on the fire. The oil and resin are cooked together, by the aid of the thermometer, until they are so combined that they will not separate on cooling; this is tried by putting a drop on a piece of glass or slate and if it clouds on cooling the combination is not complete. In fact it is common to cook varnish more than this; the more it is cooked the greater becomes its viscosity; and the more turpentine it will take to thin it to the proper consistency. Viscosity is spoken of by American varnish-makers as "body," an American says a varnish has a heavy body when an Englishman says it is "stout."

Thinning. When sufficiently cooked, the oleo-resinous compound is, on the wagon, wheeled off to another room, well away from the fire, and a previously measured amount of spirit of turpentine (or benzine, or both) is slowly added with constant stirring. Varnishes are more or less colloidal solutions, and if some of these oleo-resinous compounds are thinned directly with benzine they form a swollen, gelatinous mass, insoluble in excess of solvent; while if a little turpentine is first added this makes a solution, which may safely be diluted with benzine if desired. Some makers add driers directly with the turpentine to the hot varnish, others wait until it is cool. These driers are compounds of lead and manganese.

Proportion of Ingredients. Nothing has yet been said about the quantity of oil to be added; in most varnishes it is the predominating ingredient. The larger the proportion of oil the more elastic and durable will be the varnish; the smaller the amount of oil, the harder, more lustrous, and quicker drying it will be.

Varnishes for furniture, which should be hard and brilliant, and free from the least tendency to tackiness, are made with 10 to 15 gallons of oil to the hundred pounds of resin; those for interior house varnishing contain from 15 to 20 gallons of oil; and for outside work, exposed to the weather, 25 to 30 gallons. These 30-gallon varnishes require about 32 gals. of turpentine or other thinner; 10-gallon varnishes take about 25 gallons of thinner.

Rubbing Varnish. Rubbing varnishes contain 6 to 12 gallons of oil; they are so called because they become hard enough in from 1 to 6 days so that the surface may be rubbed with powdered pumice-stone, sprinkled on a pad of felt wet with water, until all the irregularities of surface are ground away, thus forming a smooth ("level") foundation for further coats of varnish. Those which contain even as much as 20 gallons of oil will in time become hard enough to rub; after which, by rubbing with finer materials, they may finally be polished; but this beautiful finish is not as durable as the natural gloss, which is always left on work which is to be exposed to the weather. When one coat is applied over another it is always desirable to remove the gloss by lightly rubbing the undercoat, as the following coat does not stick well and smoothly to a glossy surface.

Rosin. Common rosin, or colophony, is extensively used in making cheap varnishes. It is not a natural resin, but is produced in the distillation of crude turpentine, being the residue left in the retort after the spirit of turpentine is distilled off. It is an acid substance; and before use it is made nearly neutral by combining with it about 5 or 6 per cent of lime (calcium oxide). This makes it harder, more brittle, less easily fusible. It is made into oleo-resinous varnishes very much as are the natural resins, but with much more drier added; these varnishes are softer and less durable than the former class, but are mixed with them to make mixed varnishes of low price and medium quality. For

some purposes rosin varnishes are used alone. They have good working qualities, and a small admixture of a rosin varnish to a "gum" varnish is often advantageous. They are made at lower temperatures than the "gum" varnishes; and the greater part of the tung or China wood oil that is imported is used in rosin varnishes, on account of its superior drying qualities, in which it alone surpasses linseed oil.

Turpentine and Benzine. As to the comparative merits of turpentine and benzine (heavy petrolic ether), it may be said that without doubt turpentine is the better solvent. It is held more strongly by the oleo-resinous part of the varnish than is benzine, and hence evaporates more slowly, also it is naturally slower to evaporate. When varnish is applied with a brush it is impossible to avoid slight irregularities, slight ridges and furrows, brushmarks, and if the volatile solvent evaporates very quickly these remain and show in the dried film; but with turpentine the coating remains liquid for a considerable time and these flow out and disappear before the varnish becomes viscid enough to retain its form. Other things influence this condition, but the nature of the volatile solvent is the most important factor. It should be said, however, that there are different qualities of benzine; and within a few years a comparatively heavy grade has been on the market, with a correspondingly higher boiling-point, less diffusive power, and more like turpentine in many respects; and to a great degree free from the objections which have always been urged against the lighter grades of benzine.

Pale and Dark Varnishes. To make a pale varnish it is necessary to have pale resins; but in some cases the paler pieces are softer and less valuable. The dark grades of the better kinds of resin, such as Kauri, are of excellent quality, and for many—in fact, most—purposes moderately dark varnishes are just as good as any. Even the dark varnishes (not black asphaltum) are transparent, and have an agreeable yellow or brownish red color; on dark wood they have even a better effect than paler varnishes, to which they are in every other respect equal. There are, of course, some dark resins of inferior sorts; and some of the best pale resins, such as Zanzibar, are of unequaled quality.

Baking Japans. As the hardening of varnish is due to oxidation, it follows that with an increase of temperature the process will go on more rapidly. It is equally true that the solvent will evaporate more quickly from spirit varnishes in a hot atmosphere, so that it is generally true of all varnishes. If the temperature is high enough to melt the resin of a spirit varnish, or to keep an oleo-resinous compound in a liquid state until oxidation is nearly completed, the resulting film will be non-porous. Varnishes designed for such use are called baking varnishes or baking japans; the best of them are the black japans in which the resin is partly asphaltum. These form coatings of great beauty and merit, strongly resisting both chemical and physical action. They are

baked at varying temperatures; on wood, of course, at comparatively low heat, but on metal at as high as 400° F., though 300° F. is more common. The baking usually lasts three or four hours. The objects to be japanned are commonly dipped in the varnish and put directly in the oven. Since the drying is forced by the heat it is possible to use a varnish which would not dry at all (in any reasonable time) at ordinary temperatures, and such material is likely to be somewhat indifferent to chemical action.

Japan Driers. Another class of japans, having no relation at all to the preceding, are composed of linoleates or resinates of lead or manganese, usually containing free oil, and often some resinous or oleoresinous varnish, and dissolved to a thin liquid with turpentine or more often benzine. These are also called driers; and they act by catalysis, inducing the rapid oxidation of the oil or varnish to which they are added. It is well known that lead and manganese form two classes of compounds; for example, a protoxide and a peroxide; and easily pass from one to the other. If they are present in the film in the higher state of oxidation they give up half their oxygen to the oil, then take up more from the air, and so act continuously as agents to pass along oxygen from the air to the oil. Manganese is more active than lead but each has its advantages. Driers may be made with other metals, such as nickel and cobalt, which readily pass from one state of oxidation to the other; but have no special advantages over lead and manganese. These compounds may be made by direct heating of the metallic oxides with oil or rosin, or by decomposing soaps with soluble salts of these metals. If by use of these compounds we introduce into oil even as small an amount as $\frac{1}{1000}$ of its weight of these metals, the effect is very marked. The use of too much drier is objectionable, since it is likely to continue to act, slowly of course, after the film has hardened, and in time destroy its elasticity and coherence. Driers are not used in spirit varnishes, nor usually in baking japans.

Boiling Oil. Long-continued heating causes linseed oil to dry with a gloss, and oil which has been heated with a little lead and manganese oxides is called boiled oil; the untreated oil is called raw oil. Films of raw oil take 5 or 6 days to dry hard enough to be handled; while boiled oil will dry in 24 hours. For special purposes, however, oil is boiled for a longer time, and in this way is made the varnish used on patent leather and for some other uses.

XXXII

SUGAR

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Introductory. Highly refined commercial sugar consists of sucrose. The word "sugar," as used in this article and commercially, refers to sucrose of various degrees of purity.

Sucrose is widely distributed in the vegetable kingdom; two plants, however, supply practically all of the world's sugar. These are the sugar-cane (*Saccharum officinarum*) and the sugar beet (*Beta vulgaris*). Cane is grown throughout the Tropics and in some sub-tropical regions; the beet is produced in most parts of Europe, the northern and Pacific coast States of this country and in Canada. No beet sugar is produced in the British Islands, though excellent beets have been grown there experimentally.

Other plants producing commercial quantities of sugar are certain palms and the maple tree. For the purposes of this article it is only necessary to consider the two preponderating branches of the sugar industry, the cane and the beet. These two plants now produce nearly equal proportions of the world's sugar supply.

In sugar manufacture all substances contained by the plant juices other than sucrose are considered to be impurities. The word "impurity" is used in this sense in this chapter.

CANE SUGAR

Raw Materials and its Preparation. The raw material, sugar cane, is botanically a large grass. The approximate composition of the stalks, the part of the plant used in sugar manufacture, is shown in the following table by Dr. Charles A. Browne, Jr.,[1] and represents Louisiana cane during the manufacturing season. Tropical cane probably varies but little from this analysis except as regards the sugars, fiber and water content:

[1] "Hand-book for Cane Sugar Manufacturers," Spencer, p. 50.

Water	74.50		74.50
Ash	0.50	Silica, SiO_2	0.25
		Potash, K_2O	0.12
		Soda, Na_2O	0.01
		Lime, CaO	0.02
		Magnesia, MgO	0.01
		Iron, Fe_2O_3	trace
		Phosphoric acid, P_2O_5	0.07
		Sulphuric acid, SO_2	0.02
		Chlorine, Cl	trace
Fiber	10.00	Cellulose	5.50
		Pentosans / Cane gum — Xylan	2.00
		Pentosans / Cane gum — Araban	0.50
		Lignin bodies, etc	2.00
[1] Sugars	14.00	Sucrose	12.50
		Dextrose	0.90
		Levulose	0.60
Nitrogenous bodies (Total N = .06 per cent)	0.40	Albuminoids	0.12
		Amids (as asparagin)	0.07
		Amido acids (as aspartic)	0.20
		Nitric acid	0.01
		Ammonia	trace
		Xanthin bodies	trace
Fat and wax	0.20		0.20
Pectin (gums)	0.20		0.20
Free acids	0.08	(malic, succinic, etc.)	0.08
Combined acids	0.12	(malic, succinic, etc.)	0.12
Total	100.00		100.00

The cane grown in tropical countries usually contains an average of approximately 14.5 per cent sucrose, little or no levulose (when mature) and in all less than 1 per cent of reducing sugars. The fiber ranges from 10 to 12 per cent and even higher.

The cane is propagated from pieces of the stalk, termed "seed," which are planted in furrows or in clumps according to soil conditions. The young plants sprout from the buds at the nodes or joints of the cuttings and quickly establish themselves, soon forming large clumps and thick, almost impenetrable rows. The plant matures in the dry season in the Tropics and is harvested at this time. It never reaches full maturity in sub-tropical countries and is harvested for the manufacture of sugar in the autumn.

[1] The presence of raffinose has been reported but not confirmed (G. L. S.). The reducing sugars are grouped under the term "glucose" in cane sugar factories.

The stalks are cut close to the ground, freed of their leaves and the top joints are removed at the highest one showing signs of maturity. This point is determined by the color of the stalk. The clean stalks are removed to the factory as soon as possible after cutting. In Louisiana, however, owing to danger of frost damage late in the season, the stalks are cut and covered or windrowed and left in the fields until needed. This is not feasible in the tropics, as the cut cane would soon ferment if left in the fields, and must therefore be promptly ground.

The stubble is left to produce a crop of ratoons, to be harvested the following season, and where soil and climatic conditions are favorable, several successive crops may be secured from one planting. But one ratoon crop is usually harvested in Louisiana.

Until recent years the true seed of the cane was not known to be fertile, but since the discovery that cane does produce some fertile seed, extensive experiments in the culture of seedlings have resulted in a number of new and valuable varieties of canes.

In the preparation of the stalks for milling it is very desirable that they be freshly cut and that all leaves (trash) and immature joints be removed, since the trash reabsorbs juice in the milling process, and the unripe joints contain little sucrose and much invert sugar. Unfortunately labor conditions are usually such that the cane does not reach the mills in a clean state and freshly cut.

Manufacturing Processes. These processes include the extraction of the juice from the cane, its purification, concentration, crystallization of the sugar, and the separation of the crystals from the mother liquor (molasses).

Extraction of the Juice. The milling process is used almost without exception for the extraction of the juice. The diffusion process, described farther on in connection with the beet sugar industry, is no longer used, except in perhaps a half dozen factories.

As the cane arrives from the fields, it is unloaded upon an elevator consisting of endless chains with projecting arms or upon a belt-like conveyor composed of endless chains and wooden slats. The conveyor delivers the cane into a preparatory machine called a shredder or crusher, according to its type, which tears it into shreds or crushes it. The Fiske or National shredder, the pioneer of these machines, has two corrugated steel rolls driven rapidly in opposite directions, one at a higher speed than the other. The rolls nearly touch one another and heavy springs at the bearings permit them to separate with a heavy feed of cane. This machine tears the cane into fine shreds; the juice extracted is immediately reabsorbed. Crushers also have two corrugated steel rolls driven in opposite directions but at the same speed. The corrugations are small and have sharp edges. The crusher rolls revolve very slowly, crushing the cane and expressing more than half the juice it contains. The Krajewski and Fulton are well-known types of these machines. A Fulton

crusher is shown in Fig. 309 in combination with a twelve-roller "Cora" mill.

The rind and joints of the cane are very hard and offer great resistance in milling, hence the desirability of first breaking up the cane by machines requiring comparatively little power.

Cane mills are composed of various combinations of very heavy cast-iron rollers arranged in suitable massive cast-iron or cast-steel housings. In modern installations the mills each have three rollers, and combinations of three-roller mills make up those of six, nine and twelve rolls. The entire system is driven with one or more engines. The crusher and mills shown in Fig. 309 are geared for driving with a single engine. The use of a single engine promotes economy and regularity in the milling. Hydraulic rams are usually used to regulate the pressure on the rolls. The rams are shown under the crusher and mills in the illustration.

Fig. 309.

The following dimensions are typical of the large mills now in use: Rollers 33×84 ins. long; roller shafts, hollow nickel-steel forgings; journals 17 ins. diameter×21 ins. long. These dimensions are often exceeded, though few mills are now made with rolls longer than 84 ins. The weight of such a top roller with its shaft is approximately 14 short tons.

When the hydraulic pressure is applied to the top roll, as is usual in the majority of installations, the following loads upon it are about the customary numbers: 1st mill, 375 tons; 2d mill, 400 tons; 3d mill, 425 tons. These loads are often exceeded with very strong mills.

The mill rollers are so arranged that the cane is crushed twice by each 3-roll mill, and at each successive crushing the cane passes through a smaller opening than before. The last mill is usually "set" with its back or bagasse roll and the top roll almost touching one another, or to use the factory term, "iron to iron." A curved knife or turn plate guides the crushed cane from one pair of rolls to the next. Notwithstanding the great strength of mill rolls and shafts these are often broken by the straining to which they are exposed.

Water is usually applied to the crushed cane or bagasse, as it is now termed, as it emerges from the rolls of the first and second mills. The bagasse is in the condition of a sponge that has been squeezed nearly dry and quickly absorbs the water, which dilutes a part of the remaining juice. The subsequent milling of this moistened bagasse extracts more sugar than would be obtained with dry crushing. The water is often all applied to the second mill bagasse and the thin juice from the third mill is pumped back upon the bagasse from the first. In this method, all the juice extracted by the first and second mills is pumped to the defecating apparatus for the next stage of the manufacture. This use of water on the bagasse is termed "saturation," "maceration" or "imbibition."

The final residue is known as "bagasse" or, in the English colonies, "megasse." It is conveyed directly from the mills to special furnaces, where it is burned for the generation of steam in the boilers. All modern cane factories are operated by steam.

The bagasse, with very good milling, contains about 45 per cent marc or woody fiber and less than 50 per cent moisture. Good bagasse has a fuel value of from 3000 to 4000 B.T.Us., and in some tropical plants supplies all the fuel required in the manufacture. The majority of factories must supplement this fuel with wood, coal, or oil. The cane factory requires a boiler installation of approximately 200 H.P. per 100 tons cane ground per twenty-four hours. This number depends upon the efficiency of the plant, the quality of the cane and the class of sugar manufactured.

The loss of sugar in the bagasse varies greatly in different establishments, but with an installation consisting of a crusher and three 3-roller mills, and the use of saturation water, it approximates 5 per cent sucrose in the residue or in terms of the original cane, 1.25 per cent. With excellent milling and liberal saturation (15–20 per cent water) more than 90 per cent of the sucrose in the cane may be extracted in the juice. These numbers all indicate much better results than are obtained with the average equipment.

The yield of juice by milling varies with the quality of the cane itself. Woody canes yield less juice than those of low fiber content and immature canes more than ripe, rich stalks. By dry crushing, i.e., without saturation, 75 per cent on the weight of the cane of juice may be readily obtained with the immature canes of Louisiana, whereas in the tropics it usually requires very heavy milling and liberal use of saturation water to express an equivalent quantity.

The present tendency is toward the construction of very heavy milling plants with rolls 78 to 84 ins. long and arranged with a crusher and three or four strong mills set "tandem." Great attention is paid to the foundry mixture in casting the rollers, to obtain an iron that is neither too hard nor too soft, and that will retain a slightly roughened surface that reduces the tendency of the cane to slip and clog the mill. Such mills will grind from 1200 to 1400 tons or more of cane per twenty-four hours, though

where a very large extraction is desired the smaller number is not usually reached.

Purification of the Juice. The juice as it flows from the mills is turbid and filled with impurities, both chemical and mechanical. It is first strained through perforated sheets having 400 round holes and upward per square inch. The surface of the strainer is cleaned by mechanical scrapers, which deposit the fiber and trash upon one of the bagasse conveyors, to be again passed through a mill.

Defecation Process. The next stage of the purification is the defecation process. The raw juice is always of acid reaction. This acidity is neutralized with milk of lime or with dry slaked lime, and the juice is then heated to coagulate the albuminoids.

In the ordinary method of defecation, the juice is first limed in mixing tanks, to slight alkalinity or faint acidity, according to the grade of sugar to be made, and is then conducted to defecators. These are tanks fitted with steam coils or steam jacket at the bottom. Many factories lime the juice in the defecator. The limed juice is now heated with steam. The heat is continued until a heavy blanket of scum rises to the surface and breaks or " cracks." When the cracking point is reached the heat is discontinued and the juice is left at rest for the precipitates to settle. This process separates nearly all of the albuminoids, partly by coagulation, and a part of the acids, fat wax and gums. Some lime salts are formed and persist throughout the manufacture. A part of these salts subsequently deposit upon the heating surfaces of the evaporating apparatus. If the process is conducted with care, there is no decomposition of the sugars, but with excessive liming the invert sugar is decomposed in part and forms dark, bitter compounds with the lime. These lime salts impede the crystallization of the sugar. The ripe cane frequently contains no levulose, but this sugar always appears in the molasses, even if no sucrose is inverted, and is attributed to the action of the alkalis upon the dextrose. In an acid defecation, as in making white sugar, if insufficient lime is used, inversion of sucrose occurs.

After allowing sufficient time, usually an hour or longer, for the subsidence of the precipitates, the clear juice is decanted from between the blanket of scum and the mud at the bottom of the defecator. The clear juice is run into storage tanks preparatory to the evaporation. The scum and mud, mixed together, are pumped into filter presses and the filtrate is added to the clear juice already obtained. The press-cake is used as a fertilizer or on many estates is wasted. The sugar content of the cake is reduced by either washing it with water while still in the press or by removing the cake, beating it to a cream with water and refiltering. The unwashed cake contains from 8 to 12 per cent of sugar, according to the richness of the cane and the quantity of water used in washing the mud from the defecators, and that by refiltration or thorough washing contains about 2 per cent.

The filter press is that used in other industries. A frame press of a type very generally used in sugar factories is illustrated in Fig. 18. A heavy jute or cotton cloth is placed over the grooved or perforated plate shown next to a frame, in the figure. When all the plates are covered in this way and the press is closed a series of cloth-separated chambers is formed. The muddy juice is forced into these chambers under a pressure of 40 to 50 lbs. The cloth retains the precipitates and the filtrate flows from cocks connected with channels in the grooved plates.

In the manufacture of plantation white sugar, the raw juice is saturated with sulphurous acid, then limed to faint acidity to litmus. The rest of the defecation process is conducted as already described. In making the refining grades of sugar, sulphur may or may not be used, and is not generally employed in tropical factories. An acid defecation is usually made in Louisiana and an alkaline one in the Tropics, where lime is usually added so long as a precipitate forms. The process is termed "clarification" in Louisiana.

Phosphoric acid or acid phosphate of lime is often used in the defecation, especially in making white and high-grade yellow sugars, to form a voluminous precipitate, which carries down much flocculent and some coloring matter.

The defecation may also be conducted by Deming's continuous process, in which the limed juice is heated under pressure to a temperature of about 112° C. and then passed through closed constant-flow settling tanks. These tanks are so arranged that clear juice flows from a pipe at the top while the mud is drawn off at the bottom. The settling is accomplished under pressure. A device, termed an "eliminator," separates the air and gases from the hot juice before it enters the closed settling tanks.

There are other modifications of the defecation or clarification process, but the two described are those generally used.

The Carbonation Process. The carbonatation process, described farther on in the beet-sugar section, modified as to quantity of lime and temperature conditions, is used to a very limited extent, notably in Java. In treating cane juice by carbonatation very little lime is used as compared with beet-sugar work, and also the temperature is kept below 60° C. to prevent the decomposition of the invert sugar which occurs in the presence of lime at higher temperatures.

Evaporation. The clarified juice is next evaporated to a syrup of about 54° Brix (30° Baumé). The evaporation is conducted in multiple-effect vacuum evaporators.

There are several types of multiple-effect evaporators, but the basic principle of all is the same, so only the so-called and commonly used standard type of apparatus with vertical tubes will be described. The triple effect is the combination generally employed. The evaporating vessels or "effects" of this combination, three in number, are vertical cylinders some-

what of the form of the vacuum pan shown in Fig. 310. In the lower part is a belt containing vertical brass or copper tubes through which the juice circulates, and which are surrounded with steam. This heating belt is termed the "calandria." The vessels of the triple effect are arranged so that a vacuum may be maintained in each, e.g., 5 ins. in the first effect, 14–16 ins. in the second, and 26 ins. or as high a vacuum as can be secured, in the third. Exhaust steam from the various engines of the factory is used to heat the juice in the first effect; the steam generated in boiling this juice is conveyed through the vapor pipe in the dome of this vessel to the heating calandria of the second effect. Juice is conducted from the first vessel to the second and from the second to the third. The vapor from the first effect boils the uice in the second by reason of the differences in vacuum and boiling points, and the condensation of this vapor produces the vacuum in the first vessel. In the same way the liquor is boiled in the third vessel and the condensation produces the vacuum in the second. The vacuum in the third effect is produced by a pump and condenser. The water of condensation is removed by pumps, except from the first calandria, from which it flows by gravity. The evaporation is so conducted that a stream of juice is fed into the first vessel and flows from effect to effect, gaining in density as it travels, and finally finished syrup of the desired density is constantly pumped from the third effect. This method may be extended to four vessels, which is termed a "quadruple-effect," and so on. Owing to mechanical difficulties, this so-called standard type of evaporator is not used with more than four vessels. The water from the steam condensed in the calandrias is used for boiler feed-water and the surplus for maceration of bagasse and other purposes, thus utilizing its heat.

The method of producing the vacuum will be described later in connection with the crystallization of the sugar.

The differences of vacuum and the consequent differences in boiling points of the liquors enables the multiple-effect use of the steam applied in the calandria of the first vessel. A triple-effect apparatus will evaporate a given quantity of water with about one-third the steam required to evaporate the same quantity in single effect. A surplus of steam is generated in the first and second vessels of a triple effect, so far as the needs of the apparatus itself are concerned. In European beet-sugar practice, a part of this surplus is employed in reheating juices in the preliminary stages of the manufacture. A further economy is sometimes effected by placing a surface condenser, through which cold juice circulates, in the vapor pipe leading to the main condenser.

Crystallization of the Sugar. The concentrated juice or syrup is pumped from the multiple effect to storage tanks preparatory to the crystallization of the sugar. The crystallization is accomplished in a single-effect vacuum pan such as is shown in Fig. 310.

The vacuum or strike pan, Fig. 310, is a cylindrical vessel, A, usually of

cast iron, having a dome-shaped top with vapor pipe, *B*, and connections and a conical bottom provided with a strike or discharge valve, *C*. The pan is equipped with large heating coils of copper, and steam and vacuum gauges, also sight-glasses, *D*, for watching the progress of the work, a proof-stick for drawing test samples and suitable pipe connections for syrup and molasses. The steam enters a manifold, *E*, from which it is distributed to

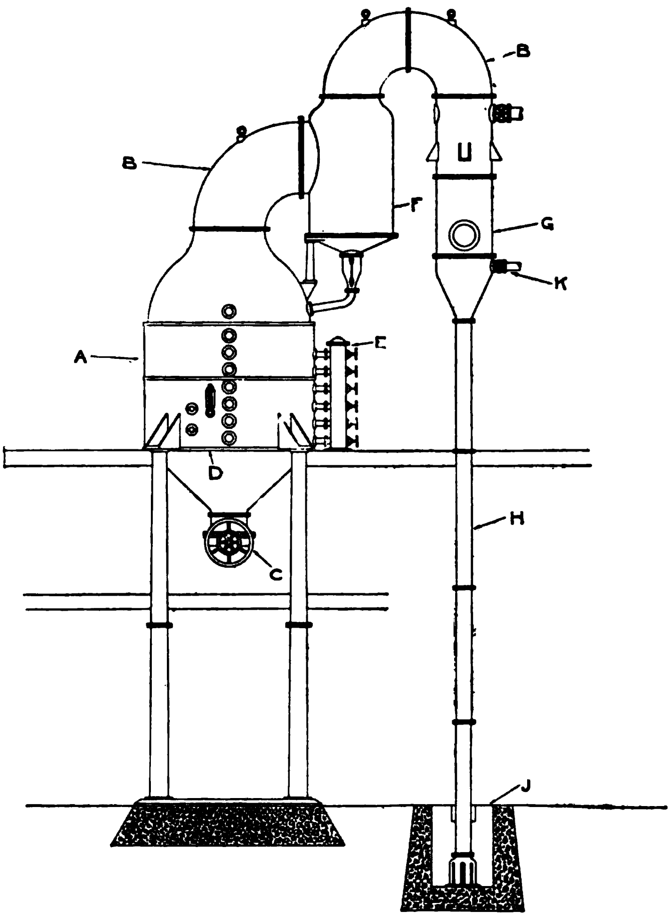

Fig. 310.

the coils; each of the latter has a stop valve, and also drainage connections for condensation water. The vapors from the boiling sugar solution pass through a save-all, *F*, connected at the bottom with the pan, where they expand and also meet baffle plates, so that sugar entrained with the vapor may be returned to the apparatus. The vapors from the evaporating liquor pass into a condenser, *G*, in which they meet a shower of water. The nncondensable gases are led off through a pipe, *K*, from the lower part of the condenser to a vacuum pump. The condensing water and water of

condensation are carried off through the " leg pipe" or torricellian tube, *H*. The foot of the leg pipe is sealed with water, in the hot well, *J*.

The above is a description of the " dry-vacuum system." It is so called because only the uncondensible gases are separately removed by the pump. In the " wet system " the condensing and condensation waters and the gases are carried off by the vacuum pump. The dry system is preferred for large installations. Many factories use a condenser in common for the multiple effects and vacuum pans.

In crystallizing the sugar, the pan boiler proceeds as follows: Having produced a vacuum in the pan he draws in what he deems to be sufficient syrup for graining the " strike," and evaporates it to a saturated sugar solution at the desired temperature. He regulates the boiling-point by the injection of water into the condenser, thus controlling the vacuum. When ready to form the crystals, i.e., grain the strike, he heats the liquor to a temperature of from 60 to 70° C., the grade of sugar desired determining this condition. At this stage there are two customary methods of procedure: In the method usually followed in the cane-sugar factories, the concentration is continued, maintaining a constant or slightly rising temperature, until crystals of sugar begin to appear in the boiling liquor. By means of the proof stick, the pan-boiler withdraws a small sample of the liquid and examines it upon a glass plate by transmitted light. He continues the concentration and these tests until a sufficient number of crystals have separated, dependent upon the grade of sugar he is making, and then admits a small charge of syrup to the pan and frees up the boiling material, being careful not to remelt the almost microscopic crystals nor to cool the liquor sufficiently to cause additional crystals to form.

In the second method of graining, the concentration of the syrup is continued until the appearance of the thread, formed by rapidly separating the thumb and finger moistened with the test sample, shows that the liquor is sufficiently saturated with sugar. The pan-boiler now increases the injection of cold water into the condenser, thus increasing the vacuum and cooling the material in the pan. The boiling mass becomes supersaturated with sugar and minute crystals immediately form. A small charge of syrup is now admitted to the pan and the concentration of the material is so regulated that no more crystals form.

It requires considerable skill in graining to form the requisite number of crystals. If an insufficient number is formed, the crystals will grow large and later in the operation there will not be enough crystal surface, and new grain, " false grain," will form, and the mother liquor will be rich in sugar. False grain impedes the subsequent process of purging the sugar and reduces the yield. Too many crystals result in sugar of too small-sized grain.

After the formation of the crystals the pan-man continues the boiling injecting syrup by charges or continuously if he so elect, to compensate for the water evaporated, and obtain a saturated solution, but always

avoiding temperature and other conditions favorable to further formation of crystals. The charges must be large enough to enable the crystals to circulate freely but not too large in proportion to the crystal surface. This forces the sugar to deposit upon the crystals already present, which soon grow to the desired size. The material is now concentrated to a solid content of about 92 per cent or more and is termed "massecuite." The steam is now shut off, air is admitted to the pan, and the "strike" is discharged through the valve into suitable recipients. In making hard grained sugars a high temperature is maintained until near the end of the operation, and on the contrary, a very high vacuum and low temperatures, produce sugars of low polarization, composed of soft crystals.

In making small-grained sugar, the crystals are formed when the pan is about half filled with concentrated syrup. "Low graining" produces a coarse sugar. If very large crystals are desired, a part of the strike is removed from the pan or is "cut-over" through pipes into an adjoining pan, and the boiling is resumed. If the cut-over pipe is used both pans may be filled with large grained sugar or one strike may continue with syrup and the other be completed with molasses to form a lower grade massecuite.

The methods described are for liquors rich in sugar and of high purity. In factories using modern methods, the mother liquor or molasses obtained from a sugar of the first crystallization is substituted for syrup, as stated above, to form a "mixed massecuite." Both the massecuite of the first boiling and the mixed massecuite are boiled to definite coefficients of purity, so that the molasses from the last boiling shall contain so little sugar that it cannot be profitably further treated for sugar extraction. In this method the pan work must be supplemented by crystallization in motion in crystallizers such as those described below. In two massecuite work, the first is usually reduced with molasses to a purity of 76° and the mixed massecuite to 60°; in the three-massecuite method, the purities are respectively about 85, 80 and 60°.

A crystallizer is a large tank, fitted with powerful mixing arms, and is made in three types, viz., closed crystallizers, open crystallizers, and vacuum crystallizers. The closed crystallizer is a horizontal cylindrical mixing vessel provided with manhole, and charging and discharging connections. The open crystallizer is similar to the closed and differs in having the upper side open, exposing a large area of massecuite to the air. The vacuum crystallizer differs from the closed in having vacuum connections and its lower half steam-jacketed. It is in fact a slow-boiling vacuum pan with forced circulation of the massecuite. The closed and open type are sometimes provided with a water jacket for controlling the temperature, but this is not usual in the cane-sugar industry.

There are many methods of using crystallizers, but a usual one in cane-sugar factories is to boil a strike of mixed massecuite, injecting molasses as described, and running it into the crystallizer. Here the massecuite is

constantly stirred during three or four days or until it cools down to the desired temperature. The crystals are kept in constant motion to bring them into contact with the sugar in solution; thus the sugar deposits upon these crystals instead of forming new ones.

Many factories still simply concentrate the molasses that is rich enough to crystallize, to " string proof," or " blank," and run it into tanks to crystallize at rest. The proof is determined as described in the second method of graining, by separating the thumb and finger moistened with the molasses, thus forming a thread, or more often, the concentrated molasses is poured from the proof stick and the appearance of the " string " formed is noted. The crystals formed at rest are small, soft and of low polariscopic test, whereas those obtained by crystallization in motion are large, firm, and of high test.

In making white sugar, sodium hydrosulphite, ($Na_2S_2O_4$), is injected into the syrup in the vacuum pan by many manufacturers just before graining. This bleaches the coloring matters and is believed to reduce the viscosity of the liquor. The bleaching effect is not very permanent and the sugars made by this and other sulphurous acid processes usually darken in color, in storage.

Purging and Curing the Sugar. The massecuite, after the completion of the crystallization, is conveyed to mixers from which it is drawn off into centrifugal machines for the separation of the molasses from the crystals.

The centrifugal consists of a shallow drum or basket, having perforated walls and lined with finely perforated brass sheets or brass wire cloth. A customary size for large machines is 40 ins. diameter by 24 ins. depth. By suitable transmission a machine of this size is rotated about 1000 revolutions per minute. A charge of massecuite is run into the centrifugal, usually while the latter is slowly revolving and the speed is then increased until the molasses is thrown off by the centrifugal force and the sugar is retained by the perforated lining.

In making raw sugar for refining, after the above treatment, the crystals are ready for packing and shipment. In the event, however, of the crystals no testing sufficiently near the market basis, 95 per cent or 96 per cent by the polariscope, according to market conditions, after all but the closely adhering molasses has been thrown off by the centrifugal, a little water is sprayed upon the wall of sugar, which quickly removes a part of the low-test molasses from it. Sugars polarizing approximately 96° are termed " centrifugals " and are the basis of market quotations for raw sugar.

Most raw sugars, i.e., sugars that must be refined before they enter into consumption, fall off in polarization during storage. This decomposition is usually attributed to bacterial activity. A loss of 2 to 3 per cent of the sucrose is not unusual during long storage of 96° sugar, and the loss is especially heavy during sea voyages. Certain districts, notably

in Java and the Hawaiian Islands, make sugars that polarize above 98° and contain little more than a trace of moisture, since such sugars suffer little decomposition during shipment and storage. These sugars are crystallized at a temperature high enough to produce a firm, clean crystal. Steam is injected between the casing and basket of the centrifugal to remove the molasses and dry the crystals or a granulator, as described for white beet sugar may be used for drying.

In making white sugar in the factory, the juice having been treated as described, the crystals are thoroughly washed in the centrifugal with water. Usually a little ultramarine is added to the water " to kill " the yellow tinge of the crystals. A granulator is often used in drying white sugar. (*See* Beet Sugar.)

The sugars crystallized at rest, from molasses massecuite, consist of small, soft crystals, which are sold on a market basis of 89° test or are remelted and reboiled to produce higher grades, or are simply mixed with high-test sugar and sold as such. All raw cane sugars are sold upon a basis of their direct polarization. Crystallizer sugars are often mingled with high purity molasses to form a magma, which is mixed and purged with the first massecuite, thus enabling the factory to produce but one grade of high test sugar.

Most modern factories inject molasses into the vacuum pans when finishing a strike started with syrup, or in some cases sugar crystallized at rest is used in the pan as " seed " in starting a strike to be finished with molasses. The object is to produce only one grade of sugar and spent molasses.

The viscous liquid residue after the removal of the crystals, the crystallization having been carried as far as is commercially profitable, is termed " final molasses," or in the markets simply " molasses." With excellent manufacture in Cuba this residue contains about 86 per cent apparent solids (degree Brix), and 52 per cent of total sugars. This latter consists of about 36 per cent sucrose, by Clerget's method, and the remainder is dextrose and levulose in variable proportions. The molasses contains about 9 per cent of ash and has an apparent coefficient of purity of about 30°, i.e., 30 per cent of the solids as indicated by the Brix hydrometer is sucrose by direct polarization.

Much lower coefficients of purity may be readily obtained in Louisiana than in the Tropics, owing to the nature of the impurities in the juice. Few tropical factories turn out molasses of lower purity than 30°, or even so low. The average yield of molasses per ton of cane approximates 4 to 6 gallons.

A few Louisiana factories do not attempt to extract more sugar than they can obtain in one crystallization, preferring rather to make a rich molasses of good color that is suitable for the baking industry and the table, the high price of this product more than offsetting the reduced yield of sugar.

The yield of commercial sugar varies with the quality of the cane, the factory equipment and management, and the grade of sugar produced. The Cuban yield averages a little over 10 per cent of the cane of sugar equivalent to 96° "Centrifugals." A few factories extract as high as 12 to 12.5 per cent. The Louisiana yield will probably average 7.5 per cent of sugar.

The following figures show the average composition of the centrifugal sugars from two very large Cuban factories which produce but one grade of product:

		A	*B*
Sucrose, direct polarization	per cent	95.90	95.73
Sucrose by Clerget method	"	96.38	96.46
Moisture	"	1.20	1.31
Glucose	"	0.97	0.92
Ash	"	0.59	0.42

Beet Sugar

Raw Material and its Preparation. The sugar beet is grown from seed. The rows are seeded thickly and the young plants are thinned to leave vigorous ones about 6 ins. apart in the row. The desirable beet is small, the topped root weighing about a pound, and is tapering, somewhat top-shaped, regular in form and has few rootlets. Large beets are not usually as rich as the small ones described.

In addition to the carbohydrates sucrose, raffinose and occasionally slight traces of invert sugar, the following organic substances have been found in sugar beets: Oxalic, formic, citric, malonic, succinic, aconitic, tricarbollicylic, oxycitric, malic and tartaric acids, chlorophyll, betaïne, asparagine, glutanine, leucine, legumine, tyrosine and the xanthine bodies, xanthine, guanine, hypoxanthine, adenine and carnine. The following decomposition products were identified by von Lippmann: Arginine, guanidine, allantonine, vernine, vicine, and in the young plant alloxanthine. The decomposition of these bodies is the source of the ammonia set free in the manufacture and drawn off from the calandrias of the multiple effect. The following non-nitrogenous bodies are also present in the beet: Lecithine, pectose, pectase and coniferine. The mineral constituents include the following substances: salts of potassium, sodium, rubidium, vanadium, calcium, magnesium, iron, and manganese and the following acids in combination with the inorganic constituents: Hydrochloric, sulphuric, nitric, phosphoric and silicic acids. Our knowledge of the composition of the beet is largely due to Scheibler, Schultze and Boshard and von Lippmann. These data are largely from an article by von Lippmann[1], also from Sidersky's *Traité d'Analyse de Matières Sucrées* and Horsin-Deon's *Traité de la Fabrication du Sucre.*

In preparing the beets for the factory, they are topped at the lowest

leaf scar and are then hauled to the factory where they are stored in sheds or in the open upon platforms, according to climatic conditions. When necessary to pile the beets in the field for any length of time, they are protected by a light covering of leaves or earth. Climatic conditions determine the methods of storage. In very cold even climates in the United States very large piles of beets have been successfully stored on open platforms. The frost affects only the outer layers, and as the thawing is gradual the beets are but little damaged.

The beets are flushed to the factory in flumes, waste water being used largely for this purpose. They are elevated to the washing machines by an apparatus which also removes many of the adhering stones and are thoroughly cleansed. From the washing machines they are elevated to automatic scales, above the slicers, for weighing.

Extraction of the Juice. The juice is extracted by the diffusion process. The washed and weighed roots are conveyed to the slicing machines, which cut them into more or less V-shaped slices or cossettes. The slices are packed loosely in the cells of the diffusion battery, which extracts the juice by a somewhat imperfect process of dialysis.

The diffusion battery consists of a number of cylindrical iron vessels, usually twelve, with suitable pipe connections, heating devices and top and bottom doors. The pipes are so arranged that the liquid may be conducted from one vessel to the next, entering at the top or bottom, at the will of the operator, and permitting any vessel to be disconnected from the series for charging with slices and discharging the spent pulp. A general view of the upper part of a circular diffusion battery is shown in Fig. 311.

In operating the battery, a vessel or diffuser is filled with beet slices, then warm water is turned into it at the bottom connection, driving out the air through a cock in the cover; by the time this diffuser is filled with water, the next one has been charged with beet slices; the direction of the current of liquid in the first is reversed, the water now entering at the top, and the thin juice, as it now is, passes into the second diffuser at the bottom, expelling the air as from the previous vessel. The thin juice is heated in transit and passes into successive diffusers as they are filled with slices. When about ten or eleven vessels have been filled, according to the number in the battery, a measured volume of juice is drawn from the last one filled, the water pressure applied at the first diffuser of the series forcing the juice to circulate. Air pressure is used in many factories, when drawing a charge of juice, to promote economy of water and sugar. The use of water is preferable, as with it the exhausted pulp may be flushed through canals to the elevators. The spent pulp is elevated to continuous presses in which a large part of its water is expressed. The juice drawn, as described, is strained through depulpers and conducted to tanks for the next stage of the manufacture.

[1] *Bul. de l'Assoc. Chimistes de France*, **14**, 691, 819.

The slices in the first diffuser of the series are now practically exhausted, but 0.15 per cent sucrose, more or less, remaining in them. This vessel is disconnected from the series and the exhausted pulp or cossettes discharged from it.

From now on each time a vessel is charged with beet slices and juice, a measured volume of juice is drawn from it and the spent pulp is removed from the first diffuser of the series, each diffuser in regular order containing the exhausted pulp. The rate of filling the diffusers depends upon their shape, size, the number in the battery and the capacity of the factory. The usual rate of filling is a diffuser of beets every six to seven minutes.

Fig. 311.

The control of the battery temperatures is of the highest importance, as the slices must not be overheated or they will mat and impede the circulation of the juice, and, besides, excessive heat favors the extraction of other bodies than sugar; deficient heat results in an imperfect extraction of the sugar. The temperature conditions vary in different factories and also with the quality of the beets. With perfectly sound beets a maximum temperature from 80–84° C. usually gives good results, but the heat must never be sufficient to soften the slices.

The volume of juice to be drawn from each diffuser must be carefully controlled. If too little is drawn the extraction of sugar is imperfect and too much unnecessarily dilutes the juice and causes waste of fuel. The usual " draw " is from 100 to 110 liters of juice per 100 kilos of beets, the quantity varying with the quality of the beets and the cost of fuei.

As may be seen from the above description, the diffusion process depends upon osmosis, the cell walls of the beet taking the place of the parchment paper in the ordinary process of dialysis. It is therefore very necessary that the knives of the slicers be very sharp, in order that as few cells as possible may be ruptured.

The exhausted pulp is used for stock food. In recent years many factories desiccate the pulp to facilitate shipment to distant markets and to permit of its use as an absorbent of liquid foods, such as molasses.

The yield of desiccated pulp is approximately 5 to 6 per cent of the weight of the beets worked.

Purification of the Juice. The beet juice always contains very fine pulp that passes the strainers of the diffusion battery. This pulp is largely removed by special strainers called "depulpers," and a part of it is carried down with the carbonate of lime in the purification of the juice.

The simple defecation process as applied to cane juice does not give satisfactory results with the beet. The juice is first defecated with lime and then the latter is precipitated with carbonic acid, hence the name "carbonatation process" is applied to the method of treatment.

The juice is run into large tanks, where it is limed; milk of lime or quicklime equivalent to about 2 to 2.5 per cent or even more of the weight of the beets of calcium oxide is added. Factories equipped with the Steffen saccharate process for the extraction of the sugar from the molasses, described farther on, use the tribasic saccharate of calcium in part, in liming.

The temperature of the juice should be from 70 to 80° C. and may reach 85° with sound beets. Formerly much lower temperatures were advised than are now employed.

The liming is followed by the double or even triple carbonatation process. Both the liming and carbonatation are usually spoken of as the "carbonatation process."

Carbonic acid is forced into the juice through distributing pipes. The lime is precipitated as a carbonate and salts of the acids of the juice. The carbonate carries down mechanically many of the impurities that have separated and also much of the coloring matter. The injection of carbonic acid is continued until the juice retains an alkalinity equivalent to about 1 to 1.5 grams of calcium oxide per liter, using phenolphthalein as an indicator. Should this carbonatation be carried too far, many of the impurities would again pass into solution. The juice foams considerably during this operation, and steam jets, oil or grease are used to beat it down. Very deep tanks are sometimes used to avoid the necessity of grease, etc.

The workman judges the end point of the carbonatation by the appearance of the precipitate in a test sample of the juice in a spoon. He is also guided by the sound of the bubbles of gas entering the juice. More accurate tests are made in many factories by titration with a standard acid.

At the conclusion of this carbonatation the juice is heated to near its boiling-point and is then filter-pressed. The filtrate flows into the second carbonatation tanks. The juice usually still contains sufficient lime, but in some factories a small quantity, about 0.25 per cent, is added. It is again carbonated, this time at a temperature near 100° C. This is termed the "saturation." The injection of carbonic acid is continued until only slight alkalinity due to lime remains. In determining this point, the alkalinity due to other alkalis than lime must be taken into account. The usual alkalinity of the saturated juice due to lime is 0.01 per cent or slightly higher.

In a few factories, the second is followed by a third carbonatation. In this event a higher alkalinity than stated must be left in the saturation. The second or third carbonatation is very often followed by saturation with the sulphurous acid gas, derived from burning sulphur. Sulphur is always used in making white sugar. In this case, as before, all but a slight trace of the lime is saturated.

Should too much lime be left in the juice from the last carbonatation, the evaporation will be sluggish in the vacuum pan, and the " strike " may even not progress at all. To avoid this difficulty, either the last carbonatation of the juice must be pushed farther or the thick juice (syrup) must be carbonated or treated with sulphurous acid. If the syrup is treated with carbonic or sulphurous acid, it must be filtered. These acids are often used simultaneously in the treatment of juice and syrup.

Filtration through presses follows each carbonatation and the sulpuring. The filtrate flows to storage tanks preparatory to its concentration.

The chemical reactions involved in the purification of the juice are complicated and not fully known.

The lime neutralizes the organic and inorganic acids and some of these are precipitated, notably oxalic and phosphoric acids; albuminoid matters are partly coagulated and precipitated. Many organic non-sugars, such as albumins, amides, amines and invert-sugar are decomposed; ammonia from the nitrogenous matter and the alkalis sodium and potassium are set free. The carbonate of calcium mechanically carries down the flocculent particles and much of the coloring matter. A little saccharate of lime is often formed, which passes into the filter presscake.

The lime forms soluble salts, many of which persist throughout the manufacture. A part of these lime salts separates during the concentration of the juice to syrup, forming scale on the heating surfaces of the evaporators. These incrustations consist largely of calcium carbonate, oxalate and a very little sulphate. Iron oxide, alumina and silica from the limestone are also deposited. Considerable organic matter also separates, including undecomposed fat and oil used in beating down foam. Lime soaps form a part of the incrustations. Raw beet sugar usually has a soapy taste and odor. On opening a jar of white sugar, a soapy odor may sometimes be noticed.

Evaporation, Crystallization, Purging and Curing the Sugar. These processes and the apparatus used are practically the same as those employed in the cane sugar industry already described.

The American factories usually produce granulated sugar. The granulator is simply a dryer so arranged that the crystals of sugar are separated from one another during the progress of the drying.

The granulator is a long sheet-iron cylinder, placed in a nearly horizontal position and arranged so that it can be revolved. Narrow deflecting plates or shelves are attached to the inside walls of the cylinder and extend throughout its length. The apparatus is inclined slightly toward the discharge end, at which are attached wire screens for sifting the sugar; there is also, at this end, a small room, one wall of which is formed of steam coils. A steam drum extends from end to end of the dryer at its axis. At the inlet end of the apparatus there is a suction fan to draw air through it and a hopper for feeding in the moist sugar. There are several types of dryers, but all depend upon the same principles.

As the sugar leaves the centrifugal machine it is elevated to a mixing floor. It is here thoroughly mixed, since all the pans of sugar and all the centrifugal charges are not of uniform color.

The sugar is next fed into the granulator or dryer, through which a current of hot air is drawn by the suction fan. The crystals are carried upward by the revolving cylinder and in falling from the shelves, through the heated air, are separated and dried. By reason of the inclination of the dryer the sugar travels to the discharge end, where it is classified by the sieves and delivered to the packing spouts.

The yield of sugar from beets, calculated to a raw sugar basis, has reached as high an average as 17 per cent of the weight of the roots in Germany and Austria. The yield is somewhat smaller in the other European countries.

The following is an analysis of a raw beet sugar: Polarization, 94.74; ash, 1.12 per cent; moisture, 1.80 per cent; glucose, none; organic non-sugar, 2.34 per cent. The high ash content as compared with cane sugar should be noted.

Extraction of the Sugar from the Molasses. In the treatment of the beet juice by the methods described, it parts with many of its impurities, yet many remain to impede the crystallization and cause the formation of the viscous after-product, molasses. The molasses from the beet has an apparent coefficient of purity of about 60° i.e., 60 per cent of its apparent solids (degree Brix) is sucrose. As may be noted in the cane-sugar part of this chapter, molasses purities below 30° are readily obtained with cane. This difference is due to the nature of the impurities that retard crystallization. Beet molasses contains about 50 per cent of sucrose and but a trace or no dextrose and levulose and about 11 per cent mineral matter, a large part of whieh consists of melassigenic salts. Cuba-cane molasses, on the contrary, contains much dextrose and levulose, about 25 per cent of

sucrose, by direct polarization, and 9.0 per cent mineral matter. Cane molasses obtained by modern methods of manufacture is not usually suitable for table use and does not contain sufficient sugar to justify the installation and operation of plants for the removal of the sugar. Beet molasses is of very disagreeable taste, is rich in sucrose, and the absence of dextrose and levulose makes the extraction of the sugar by precipitation quite simple.

Three molasses processes are now in practical use, viz., osmosis and the strontium and calcium saccharate processes.

The Osmose Process is now little used in the European factories, but has found some application in this country. As the name implies, this is a dialytic process.

The molasses is diluted with water to a density varying with its value and the cost of manufacture, and is usually such that the osmosed molasses shall flow from the dialyzer or osmogène at a density of about 35° Brix.

The osmogène has somewhat the appearance of a filter press, and consists of wooden frames separated from one another by parchment paper, thus forming shallow chambers. These chambers have suitable outlets and inlets for water and molasses so arranged that these liquids shall be separated from one another by the parchment. In operating the osmogène, the molasses solution is heated to about 90° C. and the water to 100° C. and these both are circulated through the apparatus. The operation is controlled by the density of the outflowing molasses and water charged with salts and some sugar. The density of the exosmose-water should be about 3 to 5° Brix, this number varying, however, with commercial conditions.

A part of the crystalloids pass through the parchment into the water, including some sugar. Since much of the mineral matter is crystallizable, this largely passes through the parchment, and the saline coefficient of the molasses is very much improved, also its coefficient of purity. The rise in purity permits an additional quantity of sugar to be recovered by crystallization. There is always a molasses residue with this process. Osmosis is sometimes used in conjunction with a saccharate process. The waters are usually run to waste, or may be concentrated and a part of the potash salts recovered by crystallization.

Scheibler's Strontium Process. This process is used in Europe and not at all in this country. The lack of application here is probably due to difficulty in obtaining strontianite and to conditions favorable to the lime and osmosis processes.

In Scheibler's strontium process the actual precipitation and removal of the sugar are readily accomplished, but the necessity of recovering the expensive precipitant makes the process as a whole somewhat complicated.

A solution of strontium hydrate is heated to 65°–70° C. and then sufficient molasses of this temperature to form dibasic strontium saccharate with the strontium present is added with vigorous stirring. The heating

is continued to 100° C., with stirring. The dibasic saccharate of strontium precipitates. The precipitate is collected in filters and washed with a strontia solution. The saccharate is transferred to small crystallizers, where it is cooled to 5°–6° C. and this temperature is maintained until the strontium hydrate crystallizes, leaving the sugar in a solution containing some strontia. The crystals are removed by filtration, washed with a cold solution of the hydrate, and then serve in treating another lot of molasses. The combined sugar solution and the washings of the crystals are carbonated for the precipitation of the strontium. After filtration the sugar solution is mixed with beet juice in the factory or is concentrated alone for the crystallization of its sugar.

The mother liquor on standing deposits a large part of its strontia. The residue of this, after decantation, is carbonated. The carbonate precipitated in this and the preceding operations, together with the strontia from the mother liquor, are formed into briquettes, and calcined with sufficient strontianite to compensate for the losses. After calcination the oxide is treated with water and the resulting very pure strontium hydrate solution is decanted from the sediment and the salt is recovered by crystallization.

The following chemical reaction is involved in this process:

$$C_{12}H_{22}O_{11}+2Sr(OH)_2=C_{12}H_{22}O_{11}\cdot 2SrO+2H_2O.$$

The monobasic saccharate, $C_{12}H_{22}O_{11}\cdot SrO$, was also used by Scheibler in one of his processes. There have been many modifications of his strontium processes, but in general these relate to the machinery and the methods of recovering the strontia.

Steffen's Lime Process. This method known as the "separation process," in which the sugar is precipitated as a tribasic lime saccharate, is the only one involving precipitation in use in this country. Steffen devised other lime processes, but this is the only one in extensive use.

Steffen's separation process depends upon the precipitation of a granular or crystalline saccharate. He discovered that such a precipitate is formed in the cold. The application of this process therefore involves the use of refrigerating apparatus except where conducted in winter in cold climates.

The precipitant is freshly burned quicklime ground to an impalpable powder. The molasses is diluted to about 12° Brix in a round mixer, fitted with cooling pipes, mixing arms, thermometer, test cocks and a measuring device for the lime. The solution is cooled to about 15° C. and then small measured quantities of lime are added to it at intervals with very vigorous stirring, the temperature being kept under control and at about 15° C. The temperature must be lowered after each addition of lime. After sufficient lime has been added to precipitate the sugar, with an excess to provide for that hydrated, as is noted by the density of the mother liquor obtained by filtering a test sample, the contents of the mixer are

pumped into filter presses, where the precipitate is collected and washed with cold water. The filtrate is usually rejected or a part of it is used, together with the wash water, which carries a little saccharate, in diluting subsequent portions of molasses.

The precipitate was at first thought to be tribasic saccharate of calcium, $C_{12}H_{22}O_{11} \cdot 3CaO$. The exact composition is apparently unknown.[1] When the writer visited the works at Elsdorf, Germany, to report on this process to the U. S. Department of Agriculture[2] he was informed by the chemist that the washed precipitate contains from 97 to 98 per cent of $C_{12}H_{22}O_{11} \cdot 3CaO$ and that an average of 93.4 lbs. of properly prepared lime powder is required per 100 lbs. sucrose in the molasses. The quantity of lime used depends upon its quality, fineness of the powder, and the temperature maintained in the molasses solution. A too high temperature, coarse powder or too rapid addition of the lime, cause the latter to hydrate in part. Some hydration of the lime cannot be avoided.

The saccharate of lime is used in liming the beet juice in the carbonatation process.

If the factory treats only its own molasses product, additional lime is necessary for the juice. When the quantity of saccharate is in excess of that required to supply the lime for the carbonatation, the surplus is added to a large proportion of hot beet juice and is filter-pressed, or it may be broken up in hot water. Two-thirds of the lime is removed by this treatment, and the filtrate may be used in part in diluting molasses or it may be carbonated, filtered and the filtrate concentrated for the crystallization of the sugar.

Sugars obtained by a saccharate process usually contain notable proportions of raffinose, and the peculiar shape of the crystals often observed is attributed to this sugar. It was at first thought that the raffinose was due to decompositions, but it is now known that it is derived directly from the beet itself.

Residual Molasses from the Cane and Beet. Except where a saccharate process is used there is always a residual molasses from the beet. Cane-sugar factories always produce a final molasses, the average quantity of which is about 4 to 6 gallons per ton of cane in tropical factories making raw sugar. Cane molasses is utilized in rum and alcohol manufacture and in stock feeding. Beet molasses is also used in feeding and in making alcohol. The residue from the distilleries of Europe is concentrated and the organic matter is burned, leaving an ash very rich in potash. Sulphuric acid is added to the mass before burning to reduce the loss of the nitrogen. The ash is used as a fertilizer.

Cane molasses of good color from the manufacture of white and high-grade yellow sugars is used in the baking industry and as a table syrup.

There are many small industries in which molasses is utilized.

[1] "Beet Sugar Manufacture," Claassen, Hall and Rolfe's translation, p. 213; "Beet Sugar Manufacture and Refining," Ware, Vol. II, p. 491.

[2] Bul. 5 Chem. Div. U. S. Dept. Agric.

Sugar Refining

Raw Material. The majority of the cane-sugar factories make a raw sugar testing about 95 to 96° by the polariscope and known commercially as "centrifugal sugar"; many factories also make a lower grade, a soft sugar, crystallized at rest in tanks and testing about 89° or lower. There are still a few small cane factories that do not use vacuum apparatus, but concentrate the juice until it is saturated with sugar in open vessels, then run it into coolers to crystallize. The sugar produced in this way is called "muscovado." The refining grades of beet sugar are similar in appearance to cane sugar, but have a disagreeable odor and taste. An arbitrary deduction is made from the polariscope test of raw beet sugar to ascertain the "analysis" or "titrage," assumed to be the refining value, upon which the market price is based. The deduction is usually five times the percentage of ash.

Mingling and Washing. The raw sugar is carried by elevators to mingling machines where a magma is made of it by the addition of syrup. This magma is then purged in centrifugal machines as in raw-sugar work, and the sugar is washed with water to bring it to a high test. This washed sugar is melted to form a heavy syrup and it and the washings from it are pumped to separate blow-up tanks, i.e., tanks fitted with perforated steam coils, for purification. Small quantities of lime and phosphoric acid are added to the liquor in the blow-ups and it is heated by blowing steam into it. The lime is added in proportions to neutralize the acidity of the sugar solution and that of the phosphoric acid. The refineries usually use super-phosphate of lime derived from waste bone-black treated with hydrochloric acid instead of the pure phosphoric acid. The proportions of lime and phosphate must be such that a granular precipitate forms,

Filtration. The sugar liquor flows from the blow-ups through bag filters and thence to animal charcoal or bone-black filters. The bag filters remove the mechanical impurities and the charcoal the coloring matter, also certain impurities by absorption. The high-grade liquor from the melted sugar is first run upon the charcoal and is later followed by the washings. When the charcoal no longer decolorizes the solutions properly, the sugar is washed from it with water and is largely recovered. The charcoal is dried and then heated in tubular kilns, out of contact with the air, to burn off the organic impurities it has absorbed. This is termed the revivification of the bone-black or "char." The char is used a great many times, being revivified after each use. A small quantity of new char is added from time to time to make up for loss in dust, etc. The filter bags soon fill with "mud." This is washed from the bags and together with the wash water is filter-pressed.

The water used in washing the bone black, the "char sweet water," and the filtrate from the mud presses are concentrated to a syrupy consistence and mixed with the raw sugar washings. The thin sweet-water

from the bag filter and the washings from the raw sugar packages are used in melting the washed sugar.

Crystallization and Curing the Sugar. The sugar is crystallized in vacuum pans as described for the raw sugar industries, except that as the liquors start with a very high purity repeated crystallization is necessary to sufficiently impoverish the final molasses residue. The crystals are purged of molasses in centrifugal machines.

The liquor and washings are boiled separately, the former to make two or three pans of granulated sugar and the latter to make a strike of "off-color granulated." The syrup from the granulated sugar, when of too dark color but of sufficient purity, is again char filtered and is boiled to make off-granulated sugar. The syrups from off-granulated sugars are boiled to grain and the crystallization is completed in crystallizers. This crystallizer sugar is termed "remelts" and is melted to form liquor for granulated sugar; the syrup from the remelts is disposed of as "barrel syrup."

The subsequent stages of the manufacture depend upon the grade of refined sugar to be made. Granulated sugar is made as described for beet sugar by drying and separating the crystals in a granulator or dryer. Cubes are formed in a molding machine from moist sugar and are dried in an oven. The yellow and soft white sugars are made from liquors of these colors. The yellow color of the liquors is due to repeated boiling. Loaf sugar and tablets are cut or broken from loaves or slabs molded from white massecuite.

There are many grades of refined sugar, the classification depending upon color, grain, etc.

Molasses. The molasses is reboiled for refined sugar as often as its color and purity permit. When the color is too dark or the purity is too low it is boiled to make low-grade refining sugar which is remelted and refined.

The refining residual molasses is sometimes filtered through bone-black to improve its color and it is usually sold as barrel syrup for baking and table use.

Raw-sugar factories term the concentrated juice from which no sugar has been removed, "syrup." The refineries, on the contrary, use the word to indicate a solution from which a part of the sugar has been removed, as a distinction from "liquor," a solution from which no sugar has been crystallized.

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XXXIII

STARCH, GLUCOSE, DEXTRIN AND GLUTEN

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Starch and Starch Granules. Starch is widely distributed in the tissues of the higher plants, and makes up the larger part of the solids of grains and tubers. When pure, it is a fine white powder having a density of 1.6 and at ordinary temperature is quite insoluble in water, alcohol, ether, or other common solvents. Under the microscope, starch appears as minute, white, translucent grains varying much in size and shape, but so characteristic that it is usually comparatively easy to determine their botanic origin. Morphologically, starch granules can be divided into the following groups:

1. Large oval granules, showing concentric rings and a nucleus or *hilum*, placed eccentrically, such as the various arrowroot and potato starches, the *potato group*.

2. Round or oval granules usually showing the concentric rings and having the hilum irregular, as those from peas, beans and lentils, the so-called *leguminous starches*.

3. Round or oval granules showing hilum in centre. This includes starches from wheat, barley, rye, acorns and many medicinal plants, the so-called *wheat group*.

4. Granules truncated at one end, such as sago, tapico and cinnamon starches, the so-called *sago group*.

5. Small angular grains, often polygonal, such as maize, rice, buckwheat and pepper starches, the so-called *rice group*.

The size of these granules shows great variation in different starches, being from 0.005 to 0.15 mm. or more.

The structure of the starch granule is quite complex but from the viewpoint of the chemist it can be considered as composed of a colloidal substance, *granulose* enclosed in an envelope of a more condensed substance of similar composition, *farinose* or *starch cellulose*, the latter making about 2 per cent of the substance of the granule.

If starch is heated to about 70° C., the exact point varying somewhat according to its nature and origin, it *pastes* or swells up into a pasty jelly, the viscosity of which also varies much in different starches. The micro-

scope shows this to be due to the granulose swelling through absorption of water, and bursting the granule. The granules can be gradually ruptured mechanically by grinding starch with sharp sand or in similar ways, or the "cellulose" can be removed by chemical regeants such as dilute solution of caustic alkalies or zinc chloride, when pasting occurs readily in cold water.

Classification. Commercial starches are classified according to their pasting characteristics into *thick* and *thin boiling*. The old-fashioned laundry wheat-starch is typical of the first class as a 5 per cent water mixture *pastes* into a thin translucent syrup, scarcely gelatinous at boiling temperature. Corn starch, such as sold for food, when mixed with boiling water in the above proportion, forms a practically non-fluid paste and is characteristic of a *thick boiling* starch. It is now known that these variations in pasting properties of starch of different kinds are largely dependent on the conditions of manufacture and that thick boiling starches can be made thin boiling by suitable treatment.

These properties as well as the degree of gelatinization of the cold paste are of great importance in preparing starches for certain trades. In laundry work and the textile manufactures, for instance, the demand for a paste thin enough to penetrate the fabric when hot without coating the surface and at the same time with *body* enough to give the requisite stiffness make certain types of thin boiling starches highly desirable. Thin boiling starches are also used extensively in confectionary. In other industries, as in paper box making, thick boiling starches are required.

Sources. Notwithstanding the great variety and wide distribution, there are comparatively few sources of commercial starch. By far the greatest amount manufactured in the United States is made from Indian corn (maize) which averages about 55 per cent starch and of which about 50,000,000 bushels are consumed annually in the manufacture of commercial starches and derived products. Considerable potato starch is also made in this country as well as some wheat starch, the latter being prepared from flour. Tapioca starch is imported to some extent from the far East and is used particularly in the manufacture of envelope gums. Cassava starch from Florida and the West Indies has a limited use, and is noted for the body of its paste.

Method of Manufacture. The general principles of starch manufacture are: (1) Disintegrating the plant tissue in such a way that the starch grains are set free but not ruptured. (2) Separating the gluten by diluting with water the disintegrated mixture which has previously been treated with chemicals, or subjected to fermentation, and then settling out the heavy starch by subsidence. (3) Washing the starch by agitating with water in tanks, "running" or decantation. (4) Recovery of the starch by draining in cloth-bottom draining boxes or in deep frame filter-presses. (5) Drying the starch in *kilns*.

Ordinary No. 4 corn which is commonly used in the manufacture of commercial corn starch and its allied products has according to Archbold, the following composition:

Water	11.60
Ash	1.52
Oil	5.20
Starch	54.80
Other carbohydrates	14.33
Fiber	2.09
Protein	10.46

The corn is shoveled from the railroad cars into conveyors from which it is spouted into the *steep tubs*, which are large wooden vats containing about 2000 bushels. Here it is soaked from two to four days in warm water containing about 0.2 per cent of sulphurous acid. The water is circulated through the corn and by means of an adjoining heating tank is kept at a temperature of 50° C. (120° F). The sulphurous acid seems to have a softening effect on the glutinous parts of the kernel and at the same time prevents undesirable fermentative changes. When the grain is thoroughly softened by the steeping so that the contents of the kernel can be readily disintegrated by moderate pressure, it is usually passed through a Fuss mill. This mill (see Figs. 4 and 5) in its essentials consists of two parallel vertical plates, rapidly revolving in opposite directions and carrying studs which project between each other. The corn dropping between these plates is thoroughly, although not finely broken up. The tough, rubbery germ at the apex of the kernel which contains practically all of the oil, over 30 per cent of its weight, passes out entire, and is separated from the rest of the grain by passing the mass, mixed with an appropriate amount of water, through *germ-separators*, which are tanks containing agitators so constructed that the movement brings the germs to the surface where they are removed by an appropriately placed spout and sieves, the heavier parts of the grain passing off below. The germs are drained and washed from adhering starchy liquor, dried, ground and the oil pressed out of the warm mass by means of oil-presses of the usual construction. The remaining oil cake is an excellent cattle food. It is ground into meal or shipped in the original cake, the latter, owing to its compactness and unalterability, being particularly adapted for export. The remaining disintegrated grain is mixed with water (liquor, from the separators), reground in a buhr-stone mill (Fig. 10), and the semi-liquid mass passed over the *shakers*. These shakers are inclined bolting-cloth sieves of about 200 mesh. The starch granules with most of the gluten are washed through the bolting-cloth by jets of water or starch liquor, while the woody portions fall off the lower end of the sieve. This process is usually repeated two or three times, the bran after each shaking being passed through roller mills, such as are used for grinding

flour. The bran or "wet feed" is finally passed through the *slop machine* which wrings out the enclosed liquor and is either sold for cattle feed in this moist state or it may be dried, being often mixed with the gluten meal.

The starch and gluten liquor from the shakers is agitated in tanks to keep the starch in suspension, and its density adjusted to 4–6° Bé. It is then passed over the *runs* or *tables,* which are practically level, the incline being usually only about 4 ins. for troughs 120 ft. long and 2 ft. wide. As the liquid slowly flows down the run, the heavy starch granules, rolling over each other, are practically freed from the adherent coagulated part of the gluten and are deposited upon the bottom, the gluten being carried off the end of the trough. Men with wooden paddles keep the surface of the deposited starch smooth to prevent loss of the starch through any cutting action that might be caused by irregular depositing or accidental obstruction.

The deposited starch which extends in a layer of about 1 ft. thick at the upper end of the run to practically nothing at the foot of the run is shoveled out of the troughs into cars running on a track over the top of the trough and is then dumped into the *breakers.* The breakers are tanks provided with revolving agitators, by means of which the starch may be mixed to a thick cream with water and washed once or twice by decantation according to the quality desired, or it may be purified by revolving again on the tables.

The gluten liquors from the tables always contains considerable starch which cannot be recovered as commercial starch. The liquors, therefore, are settled to remove the excess of water and the residue passed through filter-presses, the cake thus formed being ground, dried and sold as gluten meal. According to Kaufmann it has the following composition:

Moisture	9.74
Protein	31.20
Fat	2.35
Carbohydrate	54.67
Fiber	1.44
Ash	0.60

This gluten meal is often mixed with corn bran to form *gluten feed.* The starch milk is either run into *molding boxes,* wooden frames with cloth bottoms, to drain off the water, or filter-presses with deep frames are used.

Drying Methods. The starch is either dried in trays forming *pearl starch,* or *boxed,* packed tightly in paper lined boxes, and then the partially dried cake transferred to the drying kiln. The kilns are of various designs. Some are in the form of wooden tunnels through which the cars containing the starch are pushed along by the cars of wet starch entering at one end, the cars of dry starch being taken out at the other. The temperature

varies considerably at different parts of the kiln and depends on local factory practice, 160–180° F. being the customary temperature for pearl starch, the drying taking eighteen or twenty hours. Lump starch which is *boxed* is allowed to dry partially at a much lower heat, the blocks turned out of the frames being placed on shelves in a kiln the temperature of which is about 130° F. A yellowish crust which is about ¼ in. thick forms on the outside of the blocks; this is removed and the mass of clean, white starch again returned to the kiln where it is dried for several days at a temperature of about 160° F. During this drying the lumps split up into miniature basaltic like masses technically known as *crystals*. The size of the crystals can be regulated by the temperature; a low heat giving larger and more irregular lumps.

Starch when air dried contains from 12 to 15 per cent of moisture, and if more thoroughly dried in the kilns it will soon absorb water when exposed to the air until the above percentage is reached. The moisture in starch varies also with the humidity of the air; starch dried by heat being one of the most hygroscopic substances known.

Alkaline Starches. The description given above applies specifically to the manufacture of the so-called *neutral*, thick-boiling starches, and in general to corn starch. In making *alkali* starches, caustic soda is added to the starch and gluten liquors before running so as to make the gluten more soluble. Such starches have less nitrogenous impurities but are high in ash, as it is impossible to wash all of the alkali out. Alkaline starches give thicker pastes than neutral starches made by the *sweet* or sulphite processes.

Thin-boiling Starches. *Thin-boiling* starches are made by subjecting the starch to a treatment with very dilute acids at temperatures below the bursting point of the granule, usually 35–50° C. This causes an incipient hydrolysis of the contents of the granule, but does not perceptibly affect the enveloping *starch cellulose*, the dried product being indistinguishable from the original starch, even by careful microscopic examination. A certain very small amount of the granule contents is rendered soluble and can be removed by washing the starch with cold water and filtering. The amount and nature of this soluble carbohydrate, which can be detected by adding a drop or two of a very dilute iodine solution, depends on the extent of the acid modification.

Two general methods of making thin-boiling starches are used in factory practice—the first, known as the *drying in* process consists in adding either sulphuric or hydrochloric acid in very dilute form, usually about 1 per cent upon the weight of the crude *green* or *mill* starch as taken from the runs mixed with water. The excess of liquid is then drained off and the starch allowed to dry gradually at a gentle heat. This process has been practically superseded by the *in suspension* process in which case the green starch is dumped into a tank of hot water containing 0.1–0.2 per cent of acid and kept in suspension by means of agitators.

When the process is complete, as shown by pasting tests, the acid is neutralized, the starch is drained and then dried in the usual manner. These thin-boiling starches are now made in large quantities, having largely taken the place of wheat starch in the laundry trade.

Potato Starch. Practically all of the starch used in Europe is made from potatoes. Potatoes contain only from 17 to 20 per cent of starch but the actual yield per acre is more than either corn or wheat, for the reason that the potato yield is 6½ tons per acre against about 25 bushels for corn and 31 for wheat, or less than a ton of grain.

The potatoes are soaked in vats of water for several hours and then washed in a long trough containing a spiral stirrer which tosses them about thus giving a thorough rubbing. Some factories use revolving cylinders for the same purpose. The potatoes are then introduced into rasping machines equipped with rapidly revolving knives; the pulp thus formed being passed through sieves to remove the fiber and the filtrate allowed to settle. The lower layers of white starch are drawn off and the upper gray layers still containing some fiber are received and settled, this being repeated several times. The starch is then purified on *runs* and dried in a similar manner to corn starch.

Potato starch is often made thin-boiling by methods analogous to those used in corn starch modifications. Certain patented processes designed to purify the starch by oxidizing the nitrogenous compounds by use of potassium permanganate and other oxidizers also produce thin-boiling modification. Commercial potato starch usually contains about 20 per cent of water.

Wheat Starch. Wheat starch is usually made from flour, either by the old-fashioned method of allowing the mixture of flour and water to ferment in vats and then purifying the starch by settling, in which case the gluten is destroyed by fermentation and a thin-boiling starch results, or by the Martin process in which the gluten is saved and a thick-boiling starch produced. In this latter process, masses of dough made by moistening the flour are placed in a special kneading machine in which the dough is kneaded by grooved rollers working in a swinging frame, the starch being washed out through sieves by jets of water, settled and passed over runs. The resulting starch when dried and finished is thick-boiling and the gluten, still containing several per cent of starch which it is impossible to remove mechanically, is recovered as a rubbery mass.

Rice Starch. Rice starch is made to considerable extent in Europe. There are several processes, but they all depend on destroying the glutinous matter by alkali or fermentation or by both. About 0.3 per cent of potash is usually employed, the steeped grain then being ground and the starch removed by sieving and settling, the last process being a tedious one owing to the minuteness of the granules.

Tapioca and Arrow-root. Cassava (tapioca) and arrow-root starches are made from tubers of tropical plants by processes similar to those used

in potato starch manufacture. Certain varieties of the cassava plant contain large amounts of prussic acid. As such starches are used extensively for food, it is necessary that they undergo a special fermentation and washing to remove this poisonous principle. Sago starches are made from the pith of certain palms and are imported in the form of dry pellets of starch paste. Tapioca is often prepared for the market in a similar way. Cassava starches are noted for the great thickness or body of their pastes.

Commercial Glucose and Other Products of Starch Hydrolysis. Starch, according to Brown and Morris, is a highly condensed hexose carbohydrate of the formula $(C_6H_{10}O_5)_n$ consisting of approximately 100 anhydride groups which can be resolved by suitable hydrolytic agents into as many equivalents of dextrose, providing the hydrolysis is sufficiently prolonged. Dilute acids will produce complete hydrolysis the rate depending on the nature of the acid and varying approximately as the concentration, but increasing rapidly with rise of temperature. When starch paste is subjected to the action of an acid, it is gradually resolved into simpler carbohydrates, the reaction being the result of the breaking up of the numerous anhydride groups of the complicated starch molecule with the formation of hydroxyl radicles from the water present, the acid not going into the combination, but acting catalytically.

The speed at which this hydrolysis proceeds depends on the amount and nature of the acid and the temperature. If the hydrolysis is carried to completion, the final product is a glucose sugar called dextrose, although in actual practice, some small quantity of decomposition products are usually formed. The intermediate hydrolytic substances are very complicated, but behave chemically and physically as molecular aggregates of three bodies—dextrose, a biose sugar known as maltose, and a dextrin with the properties of the original starch paste.

This progress of the hydrolysis, or *conversion* of starch paste manifests itself by characteristic chemical and physical changes. The thick paste loses its colloidal nature and rapidly becomes more limpid, the density of the solution increases, although the dissolved carbohydrates become specifically lighter, and the solution becomes distinctly sweeter in taste. If tested with a weak aqueous solution of iodine, the deep sapphire blue given by the original starch paste changes as the hydrolysis proceeds, passing into violet, then to a rose red which in turn changes to a reddish brown which grows steadily lighter until just before complete hydrolysis is reached it disappears altogether. A few drops of the solution poured into strong alcohol gives a copious white precipitate during the early stages of the conversion; as the hydrolysis continues the amount of precipitate becomes less until near the end when no precipitate is produced.

If the conversion products are tested polariscopically, it will be found that there will be a progressive fall in specific rotation values from that of starch paste (202°) to that of dextrose (52.7°). The Fehling test

shows no copper reduction with starch paste, at the beginning of the hydrolysis, but progressively increases till the maximum reducing power is reached when all of the converted products are finally transformed into dextrose.

Since the discovery of the process of converting starch into dextrose by the action of heat and acids, as long ago as the beginning of the last century, dextrose in a crude form and known as *starch sugar* or *grape-sugar* has entered more or less into commerce, but its importance as a product is small as compared to that of glucose which latter has been developed in the past thirty years and become practically indispensable in many food products.

Glucose. The term "glucose" as used to define this product must not be confounded with dextrose or its isomers, but has reference to a special commercial sirup which is always sold under this designation. The name "corn sirup" which has been suggested would seem to be a happier designation, as is the German "Starkezucker sirop." It is a thick, viscid sirup, practically clear and colorless, or of light amber tint, and is a product of the partial hydrolysis of starch. Its composition varies somewhat but the average product has a specific rotation of about 135°, with a Fehling reducing value of about 50 per cent that of dextrose.

The above corresponds to a composition peculiarly well adapted to the commercial requirements of glucose, which are, that it be a practically "*neutral*" (flavorless) sweet sirup, uncrystallizablewhen highly concentrated and capable of forming uncrystallizable mixtures with cane sugar when the latter is added in large proportion. The sirup also must be capable of being refined so that it is practically colorless. The properties which make glucose valuable in the manufacture of candy, preserves, jellies, sirups and similar food products, are those of a hydrolyzed product which is converted only so far that at least 25 per cent of dextrin still remains in the carbohydrates. If less dextrin is present, the dextrose tends to crystallize out at high concentrations, while it will not adequately prevent *graining* in sugar mixtures. If the conversion is not carried to about this point, the glucose has not the requisite sweetness, while at the same time the preponderance of the less soluble dextrin makes a cloudy, pasty sirup.

A better comprehension of the chemistry of commercial glucose can be had by a study of the following diagram, which gives the variation in percentage of the three primary constituents, dextrin, maltose, and dextrose, present in the carbohydrate matter as acid hydrolysis proceeds, the progress of the hydrolysis being shown by the change in optical rotation from that of starch paste to that of dextrose. The stage of hydrolysis most favorable for the manufacture of commercial glucose for ordinary purposes lies between the rotation values, 120 and 140; although glucose used for special brewing purposes may be somewhat outside these limits. (See diagram, page 681.)

Manufacture of Glucose. Glucose is manufactured on a large scale in this country conjointly with starch, gums, dextrins and numerous valuable by-products. Practically all of the commercial product is made from corn (maize), what is known as "No. 4" being usually taken although all grades are used. The following diagram outlines the process and will assist in following the steps, which as far as the production of the *green* (crude) starch are identical with those of corn starch manufacture which has already been described.

SCHEME OF GLUCOSE MANUFACTURE

```
                               CORN
                                |
                               Steep Tubs
                                |         \STEEP-LIQUOR
        Germ Seperators—Fuss Mills            \
           |                    |                Evaporators
        Oil Presses            Buhrstone Mills  /
         /  |                   |              /
        /  (OIL)               Rolls          /
       /                        |            /
 (GERM-MEAL)                   Shakers—WET-FEED (bran) Slop-machine
                                |
                               Starch tables
                                |  ("runs")
                               / \
                              /   \
               Filter presses  ("GREEN" STARCH)
                /                   \
             Dryers                 Breakers
              /                      |
           Mills                    Converter
            /                        |
   (GLUTEN-MEAL)                    Neutralizer
                                     |
                                    Evaporator
                                     |
                                    Bag Filters (BAG LIQUOR)
                                     |
                                    Bone-char filters
                                     |          (LIGHT LIQUOR)
                                    Evaporator
                                     |          (SWEET-WATERS)
                                    Bone-char filters
                                     |              (HEAVY LIQUOR)
                                    Vacuum pan
                                     |
                                    FINISHED GLUCOSE
```

Originally, glucose was made in open *converters* which were large tubs provided with steam coils and agitators; but owing to the fact that the speed of hydrolytic action is increased enormously by temperature rise,

and as converting at high pressure effects great economy of time and acid, the open converter has become obsolete. Thus in recent years the pressure has been greatly increased, and the time of conversion reduced by three quarters or more. Hydrochloric acid is almost universally used as the hydrolyte owing to its greater converting power and because it gives a brighter, more easily refined product.

The green starch is taken directly from the tables to the converter being shoveled off the runs, and mixed with water in a *breaker*, a tank with an agitator, to a thick cream usually standing about 20° Bé.

Horizontal Converter. The older type of converter, which is still in use, is a horizontal cylinder usually made of gun metal or copper. The diluted acid is introduced, steam is then turned on and a pressure of about 30 lbs. maintained. The starch liquor is then gradually pumped into the converter in a fine stream, twenty minutes or half an hour being consumed for filling. This allows time enough to permit the entering starch to become sufficiently hydrolyzed, to prevent pasting; otherwise, large clots would be formed, plugging the apparatus and causing *freezing*. The conversion is then continued under pressure of about 30 lbs. until iodine tests made on small samples withdrawn from the apparatus show that the proper conversion point has been reached, which usually takes from fifty minutes to an hour.

Vertical Converter. In the more modern type of converter, which is similar in construction but vertical, the starch milk is mixed with part of the acid before introducing into the apparatus and is thus partially hydrolyzed in a separate tank, a larger proportion of acid being used. The whole charge is run in a few minutes into the hot converter through a large opening in the top, the cover immediately screwed on and the steam pressure quickly raised to about 50 lbs. Owing to this high pressure and the greater strength of acid used the starch is almost immediately liquefied thus causing the whole conversion to be completed in about ten minutes.

The converted liquor is turbid from the colloidal albuminoids it contains and has a density of about 16° Bé. It is immediately blown out of the converter into the *neutralizer* which is usually a large covered wooden tank provided with a stirrer and also having ventilating shafts for the removal of hot vapors. Here it is treated with a dilute solution of sodium carbonate which not only neutralizes the acid, but at the same time coagulates the colloidal albuminoids and precipitates the dissolved iron so that a bright filtrate is obtained.

From the neutralizer, the liquor goes to bag-filters of the type used in sugar refining (Taylor filters). The practically clear amber-colored *bag-liquor* usually goes thence to the bone-char filters for its first decolorization, but often it is first subjected to a further treatment with precipitants and filter-pressed before going to the bone-char.

Char Filters. The bone-char filters are identical with those used in sugar refining, being vertical cast-iron cylinders containing 20 tons or

more of char, but greater care has to be taken in the preparation of the char and in the filtering since all those impurities which affect the color, appearance, flavor and give other objectional qualities must be removed at this stage, if at all, as they cannot be collected in the mother-liquor by crystallization as in cane sugar refining.

Since the slightest trace of caustic lime or other alkali in the char will cause a brown coloration in the hot liquor, it is necessary to subject the char in the filters to a careful preparation known as *tempering*. This consists in a treatment with dilute hydrochloric acid, washing with hot soft water and a partial drying by means of steam or compressed air. This neutralizes the alkali which is present consisting principally of caustic lime and ammonia and also removes considerable of the soluble salts, especially those of iron.

The glucose is passed twice through the bone-char filters, the first passage follows bag-filtering resulting in what is known as *light liquor*. This liquor is evaporated in a multiple effect apparatus to a density of about 30° Bé., and again goes to the bone-char filters, when the product is known as *heavy liquor*. The method of procedure is as follows: The fresh bone-char as it comes from the kilns is cleaned from the dust and smaller particles which would cause clogging of the filters. It is then spouted in through a manhole until the filter is filled to within 2 or 3 ft. of the top. The hot tempering acid is then added until the char is covered, and is allowed to remain in contact with it for some time. The acid water is then drained out of the bottom of the filter and the wash water introduced, which is also drained out at the bottom. The drainings are then blown out with steam or compressed air. The filter is now filled with hot, heavy liquor which is allowed to stand for some time in contact with the char. The liquor is then slowly displaced by more heavy liquor entering at the top of the filter, the filtered liquor passing out through the bottom by means of a pipe which rises nearly to the top of the filter, thus keeping a constant level just over the upper surface of the char.

After the heavy liquor has been running over the char continuously for four or five hours, the time depending on the working of the filter and other factory conditions, the last filter full is displaced by the light liquor which then runs through the filter in the same manner for several hours. By the end of this time the capacity of the filter for efficient work has been reached, and it is now *sweetened off* by displacing the light liquor which remains in the filter by soft water, continuing the flow till a Beaumé-spindle test at the exit pipe shows that all the liquor has passed. These "sweet waters," together with the washings of the bag-filters are concentrated in an evaporator and usually put into the bag-liquors. The filter is now washed for a number of hours by a reverse flow of hot, soft water, the water entering at the bottom and passing out at the top of the filter. After this washing the char is dumped through a manhole in the side at the bottom of the filter and is carried by conveying machinery to the kilns

where it is dried by passing over hot flues in the upper part of the kiln and then heated to dull red as it passes through the tubular iron retorts. These tubes are placed vertically in the kiln and are connected to sheet-iron tubes extending out through the bottom of the kiln which serve to cool the char. The retorts and coolers are kept entirely filled with the char which is made to pass through them very slowly, at regular intervals, the char being removed in small quantities from the bottom of the coolers. In this way a large part of the organic matter which clogs the pores of the char is volatilized or destroyed without injuring the char itself. After passing through the kilns and sifted, the char is again ready for the filters. There is necessarily some loss in this *revivifying*, 1 per cent or more being removed by the sieves in a state too fine for use in the filters. This *spent char* is of considerable value, however, as it is used in the manufacture of fertilizers, colors, and for other purposes.

The practically colorless heavy liquor coming from the bone-char filters is now ready for the final boiling down in the vacuum-pans whence it comes as finished glucose and is run into the barrels for shipment.

As glucose liquors, even in the vacuum-pan, will color somewhat when boiled to the concentrations required of the commercial product, it has been the practice to inject a solution of acid sodium sulphite (*bisulphite*) for the purpose of bleaching during concentrating in the vacuum-pan. The bisulphite also acts as a preservative of the thinner sirups in which glucose was used. It further prevents, to a great extent, its darkening in the kettle, when used in hard candy manufacture. Since the enforcement of the Pure Food Law in this country in 1907 use of sulphite in any appreciable amount has been forbidden in glucose for food,[1] so glucose made since the enforcement of this law has had a light amber color.

All refined glucose contains to a greater or less extent, depending on the quality of the refining, certain impurities which cause objectionable color, flavor and odor, present it is true, in very small quantity, but still significant as affecting the value of glucose for many purposes. It is now known that these are actually impurities and not inherent in the carbohydrate, being in the main nitrogenous decomposition products from the small quantities of gluten left in the starch and resulting from its acid hydrolysis in the converter. The effect of these objectionable impurities, particularly the color, has been mitigated by the use of sulphites, which, more or less temporarily, bleach the goods and also mask to some extent the objectionable odors and flavors. Now that the use of sulphites is prohibited in glucose used as a food, manufacturers have been obliged to use starch which has been especially purified by washing or rerunning on the tables. Rerun alkali-process starches have been used, giving a somewhat better product but they have the disadvantage of increasing the mineral content of the product, owing to the alkali introduced which

[1] Temporarily pending investigation of this matter the government has permitted the use of sulphurous acid compounds in sirups up to 0.035 per cent.

cannot be completely removed and also because of the greater amount of hydrolyzing acid required.

Duryea has patents for preparing a pure modified starch for glucose manufacture in which the purification is accomplished by a mild acid hydrolysis and subsequent removal of the hydrolyzed impurities by the usual methods, such as washing or rerunning.

Glucose is usually made at th.ee concentrations, 42°, 43° or 45 Bé., and, as has already been stated, as a rule, is converted to a point represented by a specific rotation for the anhydrous carbohydrate of about 135° D. Apparently, there is no attempt to vary the composition of the product for special trade uses as could easily be done to advantage, but the lighter-colored pure glucoses are selected for confectioners' use, irrespective of the degree of conversion. Glucose used for the manufacture of table sirups is usually known as *mixing glucose.* The other principal uses of glucose are in the manufature of jellies, preserves and in brewing, although its applications are multifarious in many industries where it does not enter as a food product, as for instance, it is used in enormous quantities to fill sole leather and tanning extracts.

Grape-sugar. Grape-sugar is the name applied to a crude dextrose which is manufactured in considerable quantities in this country and is used chiefly in the manufacture of sparkling ales in brewing, also as a reducing agent in many industries, as in indigo dyeing, and in silvering cn glass. It contains from 70 to 80 per cent of dextrose, the balance of carbohydrates being those of the lower hydrolyzed products. Grape-sugar is not much used in food products owing to its bitter, unpleasant flavor, largely due to the effect of the greater degree of hydrolysis on the nitrogenous impurities of the starch already referred to and also to the decomposition products arising from the prolonged action of the acid and heat on the carbohydrate itself. The initial steps of grape-sugar manufacture are the same as those of making glucose, except that more hydrolyzing acid is used, and the conversion is carried to the point that no dextrin is precipitated when the sample is poured into strong alcohol.

As it appears in the market, grape-sugar is a hard, waxy solid, being in the main in the form of *concrete*, compact masses of crystal plates of the crude dextrose monohydrate, made by pouring the highly concentrated liquors into molds. When fresh, it is usually quite white, especially when bleached with sulphite, but it darkens with age, and the lumps become very hard. Two grades of this quality of grape-sugar are on the market, known respectively as *seventy* and *eighty* sugar, the figures being supposed to represent the per cent of dextrose in the goods.

About 1880, Dr. Behr invented a process for making anhydrous dextrose in a commercial way, and this sugar is now made to some extent. The process consists in starting a crystallization in aqueous solutions of commercial dextrose, under favorable conditions of temperature and concentration, with *seed* or pure anhydride obtained by crystallization

from alcohol. The anhydride thus obtained is in fine needles which are practically chemically pure, and can readily be purged from the mother-liquors, from which the darker, *Climax*, sugars are made for brewing purposes.

Malt-glucose. In Japan, glucose has been made for centuries by primitive methods of converting the starch of rice and millet. *Midzu-ame*, as it is called, in its better grades, is a light yellow transparent sirup resembling our commercial glucose, and by analysis it is shown to be a practically pure diastase-converted starch product. In Europe, similar sirups have been made to some extent, and practically unrefined sirups made from ground malt and other grains, known as *malt-extracts* are common pharmaceutical preparations in this country. Commercial glucose made by use of malt has not yet been put on the market as a regular product of starch. One reason for this has been the relatively large amounts of malt necessary for conversion which made the cost of production prohibitive. In 1903, Duryea took out patents for an improved method of making malt-converted glucose, in which the process starts with a purified starch, which is liquefied by an acid hydrolysis of short duration before the malt infusion is applied. In this way a very small amount of malt extract is required and a conversion obtained which gives a product practically identical with that obtained from a normal disastase conversion, but very small quantities of dextrose being present.

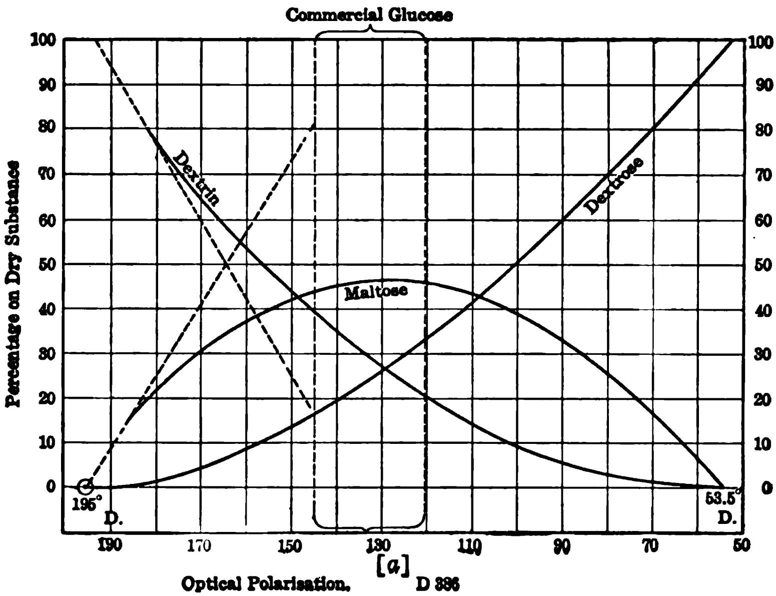
A malt glucose thus made is odorless and practically free from flavor, the objectionable nitrogenous by-products formed by acid hydrolysis apparently not being produced in this method of conversion.

Dextrin and British Gum. Artificial gum made from starch and known as *dextrins* and *British gums* are made in large quantities both in this country and Europe, and are employed in many ways as substitutes for natural gums such as tragacanth or gum arabic. Enormous quantities of these starch gums are used in the textile industries, for envelopes and postage stamps. These products are made by heating (*roasting*) starch in revolving cylinders, which are heated directly by a furnace or by an oil-bath, or in shallow trays in shelf kilns. The temperatures used vary much according to the product desired, varying from 170 to 270° C. In making dextrins, lower temperatures are used and the starch is moistened with dilute acid, usually nitric, 0.12 per cent previously to heating so that in the earlier stages of heating, considerable hydrolysis takes place. In making British gums usually no acid is used, but the temperature employed is higher, and even in this process hydrolysis first takes place to some extent, owing to the moisture and acid naturally in the starch. The time of heating varies much according to the product, white dextrins taking but two hours, while British gums are heated for fifteen hours or even longer. There are no exact standards for dextrins generally recognized, color and body of the mucilages which measured quantities of these gums make are usually the best means of their valuation. These

products are not definite chemical compounds, neither are they made according to fixed methods of procedure. Often different products are blended to give the properties desired. Little is known of the chemical constitution of these products, however much has been assumed. They contain some products of acid hydrolysis, it is true, but they are not in the main identical with products of acid hydrolysis.

Soluble Starch. Soluble starch is starch which has been but lightly dextrinized, and is practically identical with many so-called white dextrins. Actually there is no exact limit in the hydrolytic stages between soluble starch or dextrin and thin-boiling starches, as certain of the higher converted thin-boiling starches contain considerable substance more or less soluble in cold water, but there is an exact practical distinction. Soluble starch disintegrates in cold water into a smooth colloidal paste, whereas thin-boiling starch immersed in cold water preserves the form of its granules unchanged, and when dried at temperatures which do not affect the granules, preserves its original appearance.

So, too, it is practically impossible to subject commercial starch to any action of washing or other treatment with water or heat without subjecting it to more or less incipient hydrolysis which can be recognizable by appropriate physical or chemical tests. Hence, as already stated, most commercial starches show certain evidences of hydrolysis usually incipient, it is true, and dependent on the method of manufacture. At the same time there is a clear distinction between what is known in the trade as *thick-boiling*, *thin-boiling* and *soluble* starches which is based on the behavior of these products under various tests of their properties as applied in the industries.



XXXIV

BREWING AND MALTING

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Brewing is the process of preparing hopped, fermented beverages, such as lager beer, ale, stout, weiss beer, the materials usually employed being barley-malt, hops, and water.

Malting is the process of preparing cereals, usually barley, through germination, for purposes of conversion and fermentation.

Prehistoric. One of the earliest fermented beverages known to tradition, *mead*, was prepared from honey-water, that is, the washings of honey combs; hence, according to Arnold, the Latin designation for beer. Cerevisia from the Celtic Keirwysg; (Keir = wax; Wysg = water, and not from Ceres = cereals and vis = vigor); "this word was simply retained after cereals were used with the honey and even after cereals were used alone." [1]

What Beer was and is.[2] There is no legally fixed definition of the article or term "beer"; its manufacture and sale come under the provisions of the United States Food and Drugs Act of 1906, where it is classed as a "food." National and State committees and associations on food standards have wrestled with the problem of what beer is long and often, but their labors to propose a satisfactory standard have thus far been fruitless, and all beer standards have therefore remained tentative ones up to the present time.

Beer of Old—Norse, Teutons, Germans. From ancient times down to the present, the popular beverage that passed by the name of beer has been undergoing so many changes as to material employed, qualitatively and quantitatively, equipment, processes of manufacture and character of product, that it is impossible to fix a standard from usage alone that will not allow the widest latitude as to choice of materials or processes. With the older Norse and South Teutonic, or Germanic tribes, beer was a tart fermented beverage in which honey was a prominent constituent, and about the eleventh century the employment of hops became general

[1] J. P. Arnold, "Origin and History of Beer and Brewing," Chicago, 1911.

[2] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21. 1911.

on the Continent because of its bitter and aromatic and antiseptic principles and tonic effect. Later this ingredient became universal.

Cereal Base. As to cereal base, barley undoubtedly took the lead from the first, as it was the great staple article of food before wheat displaced it in breadmaking. But other cereals have had their importance in beer making in ancient as well as modern times. So China made its beer 3000 years before the Christian era from rice and millet besides barley, and in Egypt, probably as early as the building of the pyramids, millet was employed along with barley. In modern times, the variety of cereals used is much the same. In many countries, notably the United States and Great Britain, unmalted cereals like rice and corn are generally employed and sugars are favored by some; in Germany wheat is employed for some beers, and in France, Belgium and Scandinavian countries various cereal products besides barley malt, these additions to barley malt in these countries being made to secure, especially, better keeping quality and to tone down the satiating effect or richness of all-malt beverages.

The idea that the only pure beer is an all-malt beer is thus seen to be false, both actually and historically, and beer may therefore be defined as follows:

"*Beer is an effervescent beverage resulting from the thorough alcoholic fermentation of a hopped solution, in potable water, of the extractive substances principally of barley malt, together with, if desired, other prepared cereals or their natural equivalents.*" [1]

Technically, beer is a beverage properly brewed from sound materials, principally barley malt and, if desired, other prepared cereals or their equivalents; hops and potable water; with the resulting brew or wort thoroughly fermented by yeast.

Chemically, beer is an effervescent fermented malt beverage, containing in aqueous solution the products of thorough fermentation by culture yeast, mainly alcohol and carbonic acid, and a residuum of unfermented extractive substance, like dextrin, maltodextrin, maltose, albuminoids, acid phosphate, lactic acid, extracted from barley malt or other prepared cereals or their equivalents; hop bitter acids from hops; mineral constituents from the water, and the aromatic principles from hops, malt or fermentation.

Dietetically, beer is an effervescent, zest-giving, fermented malt beverage of nutrient and tonic value.

Hygienically, beer is an effervescent, refreshing, fermented malt beverage, biologically sound or wholesome, that is, devoid of and offering resistance to the development of, pathogenic or virulent microbes of all kinds.

Economically, beer is one of the greatest industrial products of many

[1] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21, 1911.

of the foremost nations. America produced during the last year over 65,000,000 barrels of beer, representing a market value of about $400,-000,000, and providing a revenue to the government of approximately $65,000,000 for the year.

Technically, lager beer is an effervescent sparkling beverage, properly brewed from sound materials, principally barley malt with, if desired, prepared cereals like corn or rice or their equivalents; hops and potable water; with the resulting brew or wort thoroughly fermented by culture bottom yeast and the fermented product stored in refrigerated cellers for sedimentation; clarified, if desired, by filtration and properly sterilized, when bottled, by pasteurization.[1]

The uniform standard for *malt liquors* tentatively adopted by a Joint Committee on Food Standards, representing the Association of Official Agricultural Chemists, and the Association of State and National Food and Dairy Departments, at a session at Mackinac Island on August 3, 1908, is:

"Malt liquor is a beverage made by the alcoholic fermentation of an infusion, in potable water, of barley-malt and hops, with or without unmalted grains, decorticated and degerminated grains."[2]

Character and Properties of Beer. Before selecting and weighing the materials in order to start brewing operations, the brewer should clearly understand the requirements the finished product is to meet and every operation he carries out should be understood with a knowledge of the influence it may have in shaping the character of the beer as desired.

A beer has *quality* if it possesses recognized merit and meets the requirements of the trade.

A beer has *character* if its properties conform to those of a recognized standard or type.

Typical beers may differ widely as to their distinctive properties. We may distinguish, for instance:

The *Bavarian* type of lager beer, with a light brown to dark brown color, malt flavor, and a sweetish taste as the main features, with the aroma and bitter taste of hops but little pronounced; usually lively and sparkling. Alcohol content about 3½ to 4 per cent. From worts of about 12½ to 14½ per cent extract.

The *Bohemian* type of lager beer, with a light yellow to greenish yellow color, pronounced hop aroma, and bitter taste; while the malt flavor is not pronounced; usually lively and sparkling. Alcohol content about 3½ to 3¾ per cent. From worts of about 12½ per cent extract.

The *Vienna* type of lager beer, with less pronounced character than either Bavarian or Bohemian types; in point of color, hop, and malt aroma, sweet and bitter taste, it takes a place between these two types.

[1] Address before the Second International Brewers' Congress, Chicago, Ill., Oct. 18–21, 1911.

[2] Wahl-Henius "Hand Book of the Brewing, Malting, and Auxiliary Trades," 1908, p. 1443.

Alcohol content about $3\frac{3}{4}$ per cent. From worts of about $13\frac{1}{2}$ per cent. extract.

The *Dortmunder* type of lager beer, with very light color; from long grown, low kiln-dried malt, hops and malt flavor not very pronounced; highly and completely attenuated. Alcohol content about 4 to $4\frac{1}{2}$ per cent. From worts usually above 14 per cent extract.

The *American* type of lager beer, with a light color, and pronounced hop aroma, less bitter than the Bohemian, with a high degree of brilliancy; quite lively and sparkling. Alcohol content about $3\frac{1}{2}$ to 4 per cent. From worts of about 11 to 14 per cent extract.

Ale, with a light color, very pronounced hop aroma, and bitter taste, and with a rather high percentage of alcohol and tart taste in the aged product, either lively or still, and usually clear. From worts of about 14 to 16 per cent extract.

Stout, with a very dark color, malt flavor and sweet taste, brewed stronger than ale, and possessing a tart taste in the aged product, but less alcohol than ale; usually lively. From worts of about 16 to 18 per cent extract.

Porter, with a dark color, brewed like stout, but not so strong.

Weiss beer, very light in color, no pronounced malt or hop flavor, quite tart, very lively, but not usually sparkling; often turbid.

Common and *Steam beer*, light in color, hop aroma and bitter taste not very pronounced; very lively and not necessarily brilliant.

All so-called lager beers, like the American, Bohemian and Bavarian types, should possess a certain degree of palatefulness, and should draw with a creamy, lasting head, which requirements are not to the same extent to be met by the other brands.

Besides the above there are brewed in America beers to meet special requirements, for instance:

Low-alcohol beers, less than 2 per cent alcohol by volume.

Non-alcoholic beers, less than .1 per cent alcohol by volume.

Tonics, so-called: bottled brewed with a high percentage of extract, usually all-malt beers, possessing a dark color, either thoroughly fermented with a high percentage of alcohol and comparatively low percentage of remaining extract, or imperfectly fermented, with a low percentage of alcohol, and high percentage of remaining extract.

Beers Classified. According to the system of fermentation employed, beers may be classified as follows:

1. Bottom Fermentation.

a. Pilsener *b.* Wiener *c.* Muencher *d.* Dortmunder *e.* American lager beers *f.* American steam beers	German lager beers.

2. Top Fermentation.

g. Mild ales and stock ales *h.* Porter *i.* Stout	English beers.
j. Cream ales Sparkling ales Stock ales Porter, and Stout Common beer	American beers.
k. Weiss beer	

3. Spontaneous Fermentation.

l. Lambic *m.* Faro	Belgian beers.

The influence of the system of fermentation on the composition of the beer becomes noticeable, especially in the different quantities of lactic acid produced during fermentation and storage.

Bottom fermentation beers have, as a rule, less lactic acid and fewer bacteria than top fermentation beers; these, in turn, have less than spontaneous fermentation beers.

Bottom fermentation proceeds generally at a relatively low temperature, viz., 43–52° F., but also as high as 45–57° F.

The designation of the two types of fermentation is derived from the fact that in bottom fermentation the yeast for the most part settles on the bottom, whereas, in top fermentation, it rises to the surface.

Bottom fermentation takes 8–16 days; top fermentation about 3–5 days.

In spontaneous fermentation no yeast is added to the wort, the fermentation proceeding slowly through ferments reaching the wort or beer accidentally.

Preservative Principles. The characteristic differences between the English and German brewers' products consist mainly in the high percentage of alcohol in the former, together with a larger amount of hops employed, the alcohol content of ales and stouts running from about 4 to 6 per cent, that of lager beer from about $3\frac{1}{4}$ to 4 per cent, that of weiss beer from about $2\frac{1}{2}$ to 3 per cent. The amount of hops employed for ales and stouts averages over 2 lbs., for lager beers from $\frac{1}{2}$ to 1 lb., for weiss beer less than $\frac{1}{2}$ lb. per barrel. The larger amount of alcohol for the English breweries' product, as well as the larger amount of hops employed, are required as preservative principles, the alcohol and hop resins having well-known antiseptic properties, while the German breweries employ refrigeration or low temperatures to preserve the beers in storage and check the growth of foreign ferments. Weiss beer, which

has a relatively low alcohol content and is produced with relatively small amounts of hops and without the application of refrigeration, shows the influences of these preservative principles, inasmuch as this product contains a large amount of lactic acid, produced by the lactic acid ferment, which is unchecked, as it were, during the production of weiss beer.

The difference in the process of production of English beers and lager beers consists chiefly in the lesser quantity of materials, both malt and hops, employed in the latter; in the low initial mashing temperatures, in lower fermentation, and very low storage temperatures (about 32 to 34° F.) and in the treatment of the beer after fermentation.

Ales and *stouts* undergo a brisk secondary fermentation on storage. *Lager beer* reaches the storage or stock cellar either thoroughly fermented and then undergoes no secondary fermentation, or it undergoes a slow secondary fermentation, in which case the beers are not chilled on storage to the same extent.

Ales and stouts that are stored for a long period are called " stock " beers. Those which are stored for only a short period, undergoing no secondary fermentation, are called " mild beers." These are usually brewed with less extract (about 14 per cent) than stock beers.

The difference in the production of *ale* and *stout* consists mainly in the characteristics of the malt and in the treatment of the product after fermentation, ale being produced from pale, or low-kiln dried malt, stout from a mixture of pale malt, caramel malt, and black malt.

Stock ale receives, after fermentation, an addition of hops in the storage cask, whereas stout receives no such addition, with the result that ale undergoes a more brisk secondary fermentation and consequently generally has a higher percentage of alcohol than stout of the same original gravity of wort, while stout contains on this account more extractive substances, and is therefore sweeter to the taste than ale.

Lager beers and *mild English beers* contain considerably less acidity than the English stock beers, which are a little tart to the taste, on account of some acidity taken up mainly during the storage period, from ferments other than culture yeast.

The amounts of lactic acid in the different beers, and which may be considered characteristic of the beers, are as follows:

Weiss beer, about	.50 per cent
Stock ales and stouts, about	.20 to .30 per cent
Mild ales, about	.15 to .18 per cent
German lager beers, about	.10 to .15 per cent
American lager beers, about	.05 to .10 per cent

The acidity in *lager beer* is not due to the development during their production of lactic acid bacteria, but to the development of this organism during the growth of the malt. Unmalted cereals, which are generally

employed in the production of American lager beers, contain no acidity, hence the low quantity of acid in these beers.

Brewing Operations and Equipment, Especially for the Production of Lager Beer. Beer is produced from the materials, mainly barley-malt, hops, water, and yeast, through the processes of cleaning and crushing the malt, mashing of the malt (with or without other cereals); straining or filtering the resulting solution, which contains the extractive substances of the materials, from the grains or insoluble portion; washing out the grains with hot water; boiling this solution, which is now termed wort, before and after adding hops; straining or filtering the hopped wort from the spent hops; cooling of the wort; adding yeast to incite fermentation; drawing off the fermented beer; clarifying and giving life to the beer; racking the beer into trade packages.

Besides these operations, which more particularly concern the character of the finished product; there are many supplementary operations necessary as precautionary measures to insure freedom of the beverage from taint or contamination of any kind, such as foreign odors or ferments, by *varnishing* of all large wooden receptacles, such as tanks and casks; *staining* iron vessels, such as hop-jack; *pitching* the wooden trade packages, such as barrels and kegs; thorough cleansing of all beer receptacles and utensils, aseptic or antiseptic treatment of all wort or beer conduits and of cellar floors, walls, and ceilings by applying suitable washes, paints or calcimine; treatment of brewing and boiler-feed water, etc.

Brewing Equipment. The modern brewery is equipped with power and refrigerating plant, while the brewing operations proper are carried out in three departments, each so arranged and equipped as to allow of a separate gravity plan of transfer of materials in each, viz., (1) cleaning and crushing of malt in elevator or mill house; (2) brewing operations in brew house; (3) cellar treatment in fermenting cellars, stock cellars, and chip cask cellars. Besides these there are provided a wash house, the pitch yard, and in many breweries the bottling department, or the bottlery.

Mill House. This contains elevators and conveyors for bringing the malt to the *malt storage bins* made either of wood, steel, or concrete, capacity up to about 10,000 bushels; *malt* and *cereal scale hoppers* of steel, round or square, provided with conical bottom; wire cloth cleaning reel; *dust collector; automatic weighing scales; malt mill* to crush malt for extraction, provided with magnets for removing particles of iron.

Brew House, Fig. 312. *Hot* and *cold water tanks; water meter* and gauge. *Cereal cookers* of cylindrical form of steel with stirrer, usually heated with live steam; *mash tun*, a cylindrical vessel of sheet-iron or steel, supplied with a removable perforated strainer or false bottom; also stirring device for mixing malt and water, a steam heating device and sparger to supply a spray of water to wash out grains, a battery of wort pipes connecting the bottom of mash tun with a copper receptacle called

the *grant; mash-tun thermometers*; *safety mash-tun gauge* to regulate flow of wort; *grains tank* of steel with conical bottom, usually outside of brew house; *grains dryer, mash tun pumps. Brew kettle* or *copper* in which the wort is collected from the mash tun and is boiled before and after hopping; usually pear-shaped, provided with a steam-jacketed

Fig. 312.

bottom. *Hop-tearing machine* and *screening machine* to separate the valuable ingredients like lupulin; *hop-jack* provided with perforated false bottom to strain out the spent hops; *wort pumps*, piston or centrifugal; *surface cooler*, a shallow iron or steel pan, allowing aeration and evaporation, causing cooling. *Wort* or *beer tank* takes place of surface cooling; *pipe cooler*, the most common being the Baudelot cooler, con-

sisting of a series of pipes arranged in vertical tiers over the outside of which the wort is allowed to flow; *enclosed* or *double pipe cooler* takes the place of the Baudelot, consisting of a series of tubes forming angular sleeves.

Fermenting Cellar. *Starting* or *settling tubs* of wood used as receptacles in which to start fermentation by adding yeast and in which the sludge or albumen, coagulated in the kettle by boiling, is separated, usually of a size to hold an entire brew. *Fermenting tubs* used as receptacles for the beer during principal fermentation; generally of cedar, holding 50 to 100 barrels and more. *Attemporators,* usually circular pipes or coils with circulating brine; suspended and immersed about 2 ft. below the beer.

Stock Cellar. *Stock* or *storage vats* or tanks are used for holding beer during after-fermentation or ripening process or for general storage purpose, usually of cedar, upright, closed at the top, capacity from 50 to over 1000 barrels; cylindrical glass enameled steel vessels are also used. *Vat supports* consisting of rails supported by cast iron legs. *Manhole doors,* either outside, closed by lugs, or opening inward, placed near bottom of vats.

Chip Cellar. *Chip casks* in which clarifying and carbonating takes place, generally built of quarter-sawed oak, usually barrel shaped, the large dimensioned ones reinforced by iron rods; also steel construction. *Attemporators,* for chip casks are often used, especially in the production of chill proof bottle beer. *Cask manhole doors; cask supports.* *Bunging apparatus* for maintaining a certain pressure on the surface of the beer in the chip cask and releasing an overpressure. *Beer filters* are used for the purpose of straining out of the beer any floating particles, such as yeast or albumen. Wood pulp serves as the filtering material, which is compressed into cakes or cells placed in a suitable copper or steel shell. *Pressure regulating pumps,* which allow any desired pressure to be put on the beer passing through the filter on its way from chip cask to racking bench, thus reducing necessary pressure on beer in chip cask and strain caused thereby. *Back-pressure racking machine,* introduced to prevent loss of gas and do away with beer overflow, entailed by old open style or racking-gut system. The beer enters through a tube inserted through the bunghole of the package, fitting air-tight, and permitting the filling of package against counter pressure. *Carbonators,* used for the purpose of charging stock beer with carbonic acid gas, usually while the beer is passing from the chip cask to filter.

Wash House. Where returned empty packages are washed. *Automatic barrel washers* soak, convey, scrub, and rinse the packages with little labor. *Barrel elevators* to raise filled packages from one floor to another or to the loading platform. *Chip washer,* a perforated revolving device for washing chips. *Filter mass washer,* a vessel in which the filter mass is washed by agitation and flowing water. *Hoop driving*

machine, pitching machine and *appliances,* to apply a coat of pitch to the interior surface of the barrels or wooden trade packages, to prevent penetration of wood by beer and consequent souring or infection. Different systems are employed. The old pitch is usually removed by

Fig. 313.

superheated steam or hot air and fresh pitch is introduced either in measured quantity, or by means of a spray, the surplus returning to the pitch kettle.

Bottling Plant. The increasing demand for bottle beer in all parts of the United States has resulted during the last ten years in the establishment of a large number of new bottleries, palatial as to magnitude

of establishment and expense of equipment typical of the technical advancement made during that period.

General Arrangement. This must be done with an eye to economy and thoroughness. There should be absolutely no useless or double handling of any bottle or case, and benches or machines should be so placed in relation to each other that they form an unbroken line from the dirty returned bottle to the capped and labeled bottle in the case for delivery.

The bottles should first be placed in the soaking device (tank or machine), from which, when all labels, tinfoil, etc., are removed, they are run through the washing machine, placed on the adjacent rack next to the filling machine, and closed either with cork, cap or patent stopper. They are then carefully examined, clamped or wired, and put in a crate previous to going into the pasteurizing tank. After being sterilized in a hot water bath, they are labeled and capped with tin foil.

In large establishments the filling from barrels carted to the bottlery across the public highway—as required by law—has been generally replaced by filling from government tanks, connected by pipe line from the chip casks directly. Here the casks or tanks, placed in a separate refrigerated room under the bottle shop, are filled and gauged under control of a government inspector.

Equipment. *Bottle soaking tanks* usually divided into compartments through which the bottles by means of endless chains are carried, filling and emptying automatically with solutions of soda and finally water. *Washing* and *rinsing machines* for thoroughly cleansing the bottle inside and outside. *Bottle fillers, bottle closing machines* for cork, patent stopper, crown, or seal. *Pasteurizing tanks,* with automatic temperature regulators, containing hot water baths in which the bottles are immersed or through which they are carried by endless chains in order to be sterilized, the temperature of the pasteurizing bath being maintained at approximately 140° F. *Labeling, dating, wiring machines.* Accessories: tin foil removers; cork extractors; steaming caps; steaming trays or boxes.

Power Plant. The consumption of fuel in the power plants of breweries is an important economic question and is receiving more expert attention of late. Breweries are therefore found that engage the best technical engineering talent and install the most efficient and up-to-date appliances for the production, transmission and application of power for heating, lighting, cooling, and ventilating.

The *boiler plant,* with its automatic stoker system; the *machine room,* with its steam engines, refrigerating machines, air compressors, dynamos, or motor generators for furnishing power and electric current for pumps, conveyors, stirrers, for arc and incandescent lamps; ventilators, etc.

Refrigerating Plant. In the production of lager beers low cellar temperatures are necessary. These were formerly obtained by employ-

ing ice for cooling the rooms but a refrigerating plant is now part of every well-equipped brewery. This plant includes the *refrigerating machine;* the piping with *condensers* and *pan;* Baudelot cooler; enclosed coolers, attemperators in fermenting vats and chip casks. The rooms to be cooled are the settling tank room, fermenting room, stock cellar, chip cask cellar, racking room, hop storage room, ice storage.

Refrigerating machines used in breweries are of the compression order, the process being practically the same for all types, the principle being based on the ability of certain gases, usually ammonia but also carbonic acid and others, to become liquid by compression and cooling, usually by water which absorbs and carries away the heat (in the condenser); and the ability of these gases to evaporate at temperatures required in the cooling pipes or coils, thereby abstracting heat from the surrounding air or liquid, thus lowering their temperature.

Brewing Materials. The materials commonly employed wherever beer is produced are *hops, malt,* and *water.* In some countries, like England, sugars and other adjuncts are used in part with malt; in the United States corn is commonly employed besides rice and sugars. In Germany the employment of any substitutes for or adjuncts to malt is prohibited. Barley is the distinctive cereal that furnishes malt, the exception being wheat used for weiss beer malt.

Malt and Cereals. Malt is produced from barley by the processes of cleaning, steeping in water, germinating on the floor or in compartments or drums, kiln drying.

Properties of Malt. The berries should be of uniform size and shape; husk and endosperm of light color; it should be free from other grain like wheat or oats, or seeds like mustard, rape; odor aromatic, not musty; growth uniform with about 90 per cent of acrospire three-quarters up; condition of endosperm mellow, not flinty; laboratory yield on dry basis about 72 to 74; moisture content not over 6 per cent, lest slackness ensue; strong diastatic and peptic power for proper inversion of starch and albumen; bushel weight not less than 34 nor more than 38 lbs.

Corn is employed with germ and husk more or less removed in the form of grits or meal in a separate cooker or in the form of flakes in the mash tun; *rice* either broken or as meal in the cooker; *wheat* in flaked condition in the mash tun or crushed (by means of malt mill) in cooker.

Malt yields about 64 to 70 per cent of extract in the brewery, of which 4 to 5 per cent are albuminoids; rice about 75 to 80 per cent, corn about 75 to 78 per cent; wheat about 65 to 70 per cent, of which 2 to 3 is albumen; rice and corn yield practically no albumen.

The employment of unmalted cereals like rice and corn offers a number of advantages. They can generally be obtained at a lower price and yield more extract than malt. They lend themselves better to the production of beers of Bohemian or Vienna types than all malt. The

resultant beers are of paler color, of greater stability when pasteurised and their brilliancy less affected by low temperatures.

The employment of wheat may not be more economical, nor are the wheat beers more stable or less sensitive to low temperatures than all-malt beers. They have a peculiar palatefulness that recommends them in some localities.

Commercial glucose and other brewing sugars are prepared from the starch of corn through inversion by acids at high heats (under pressure). They contain dextrose and dextrin in varying quantities.

Other Adjuncts. Dark malts. For preparing a beer of dark color a malt may be used which has been subjected to special treatment in the kiln, so as to acquire a dark color, such as *caramel malt*, the husk of which is yellowish brown, while the endosperm has a decidedly brown color. In its preparation, ordinary malt of good quality is steeped for a while, so as to take up a certain amount of moisture. It is then dried, and heated in suitable vessels, first to a comparatively low temperature in order to promote the formation of sugar, and later to higher temperatures at which the sugar is caramelized. *Black malt* is dried at higher temperatures, so that both the husk and the endosperm possess a blackish brown color. It does not have the pleasant caramel taste of caramel malt. The coloring power is very great. *Malt color* is an extract of black malt, filtered and evaporated to a syrupy consistency. *Roasted corn* is prepared from corn in the same manner as black from barley, i.e., by heating to higher temperatures. Its coloring power equals that of black malt.

Hops. Hops as they are used in the brewery are cone-shaped formations, representing clusters of blossoms of the female hop plant. From

FIG. 314.—Hop Cone (Unripe Stage). FIG. 315.—Hop Cone (Ripe Stage).

forty to sixty flowers are grouped together on a central spindle which is zig-zag shaped, forming a so-called hop cone or the umbel of the hop.

At the time of maturity, the seed of the hops and the whole lower and

inner parts of the bracts are covered with a fine light-yellow dust consisting of minute granules of lupulin, which contain both the bitter and aromatic principles of the hops, viz., the hop oils and resins, besides hop tannin, hop bitter acids, hop wax, nitrogenous bodies, carbohydrates and mineral substances, an enzyme (diastase) which is of special importance in ale brewing.

Up to 1808 hop culture remained confined to three New England States, Massachusetts, Vermont and Maine. Later the hops from New York State were found not only superior in quality, but three times as prolific. About 1860, small patches were planted to hops in Wisconsin and Michigan but by 1880 hop cultivation was well introduced in California, Oregon, and Washington, which States, together with New York, now furnish the hops for the American market, while large quantities are also exported.

Water. A good *brewing water* should be clear, bacteriologically pure (uncontaminated by sewage), free from odor or taste; moderately hard with a moderate amount of sulphate of lime, and common salt, free from iron and alkali. Such water is also adapted for malting; for washing of tanks, bottles and barrels, filter mass; for watering yeast, and dissolving isinglass. For the *steam boiler* the softest water is the best if free from odor; for *cooling* it should be free from acids and not too hard.

If water does not come up to requirements it may be improved by filtration, by boiling, by hardening, by supplying deficient mineral matter (Burtonizing) especially practiced in ale brewing; by softening and by purification.

Varnish. Wooden vessels in the brewery, like starting vats, fermenting vats, stock tubs, and chip casks, are varnished for the purpose of preventing any extractive matters that may remain in the wood from getting into the beer. At the same time the varnish prevents the beer from penetrating into the pores of the wood where it would sour and become a source of infection that would subsequently attack the beer run into the vessel. Varnish in general is a solution of shellac in either grain or wood alcohol properly rectified; raw wood alcohol is extremely poisonous.

Pitch. Trade packages are internally covered with a coat of pitch for similar purposes to those which lead to varnishing storage casks, etc., i.e., to prevent the beer from coming into contact with the wood. Ordinary brewers' pitch, most commonly used, is the purified resin of certain coniferous trees, as pines, firs, called turpentine. The resulting colophony is softened or made pliable by melting with some rosin oil, cotton-seed oil or paraffin.

Clarifying Chips are used at the expiration of the storage period; these being strips of wood, usually beech or maple, 6 to 12 in. in length, with a thickness one-twelfth of an inch. They should be well seasoned and carefully boiled out.

Isinglass for beer clarification is derived from fish sounds, or hide of the calf, containing gelatine as active principle.

Brewing Operations. Brewing operations proper include all operations conducted in the mill and brew house, viz., cleaning and crushing the malt; mashing; straining; boiling before and after hopping; hop straining; cooling.

Mashing Systems. Different methods of applying temperatures to a mash supply the following systems:

1. Infusion or water mash: English beers. High initial temperatures.
2. Decoction or thick mash: German lager beers. Low initial temperatures.
3. Malt infusion and unmalted cereal decoction mash: American lager beers. Low initial temperatures.

By the infusion method the mash is brought to its final temperature by the admixture of water of suitably high temperature. By the decoction method, part of the mash itself is raised to a boil and then returned to the mash tun. The unmalted grain is boiled separately with some malt and run into the malt mash to produce the final temperature.

American Brewing Operations. Cleaning and crushing the malt in a *roller mill;* mixing the grist with water, approximately 100 lbs. of malt per barrel, at 100° F., in the *mash-tun,* which contains false bottom and stirrer; holding the mash here for peptic action for about one hour; when boiling hot rice or corn mash or hot water is run in, raising temperature to about 154° F., maintaining this temperature for about 15 minutes for diastatic action, and raising to final temperature of about 165° F. in 15 minutes, resting the mash about 30 to 45 minutes; tapping; straining, when clear, into kettle; sparging the grains left in mash-tun with water of 165° until thoroughly extracted; boiling wort in *kettle* before addition of hops for about one hour, and one hour more with hops; running brew into *hop-jack,* straining out the hops; pumping wort on surface cooler, running over Baudelot cooler into fermentation starting vat, where it is yeasted. *Rice* or *corn* are generally mashed in a separate cooker together with a part of the malt, and when boiled sufficiently long the mash is united with the malt mash in the mash-tun.

American Lager Beer. *Pale Lager Beer.* Strength of wort, 12 to 13 per cent extract. Material, 50 to 55 lbs. per barrel, of which about two-thirds should be pale malt and one-third may be unmalted cereals, like corn grits, corn meal, corn flakes, corn starch or rice. Sugars like glucose may also be employed to the amount of about 25 per cent in place of unmalted cereals.

Malt Beers are brewed from 12 to 15 per cent extract, and require 50 to 60 lbs. of malt.

Pale Lager Beers should be brewed from 12 to 13 per cent extract, and require from 45 to 53 pounds of material, of which two-fifths may be unmalted cereals.

Pale Bottled Lager Beers should be brewed from 13 to 15 per cent extract, and require from 52 to 60 lbs. of material, three-fifths of which may be malt and two-fifths unmalted cereals.

Temperance Beers are brewed with about 7 to 8 per cent extract.

Malt Tonics are brewed with about 15 to 18 per cent extract.

Principles of Mashing. Mashing is the process of extracting the goods by mixing them with water at suitable temperatures and in proper relative quantities, preparatory to boiling in the kettle.

Chemically it proceeds in the main by the inversion of the starch into maltose, malto-dextrin, and dextrin, and the modification of the insoluble albuminoids into a soluble form. These changes are brought about by the agency of two substances which are contained in the malt, and begin operations when the malt is mixed with water at definite temperatures.

FIG. 316.—Mash-tun and Apparatus.

These substances are called diastase and peptase. They were formerly called chemical ferments as distinguished from the organic ferments which are responsible for fermentation. At the present day the term enzymes, or soluble ferments, is more commonly applied to them. It is the function of the diastase to invert the starch, of the peptase to modify the albuminoids of malt, as above indicated.

The amounts, both absolute and relative, of dextrin, maltodextrin and maltose, as well as of the modified albuminoids like albumoses, peptones and amides, finally present in the wort, are materially affected by the conditions under which the enzymes do their work. Hence, it is in the power of the brewer to control the composition of the wort, within certain limits, by modifying such conditions.

It generally being desirable to obtain beers with a high degree of palatefullness and foam stability, properties dependent in the main upon

the amount of unfermentable extractive substances left in the beer, among which there should be a sufficient amount of the desirable albuminoids or proteids, the mash is generally peptonized at low temperatures, for instance 100° F., for about one hour, while the starch is inverted at higher temperatures, for instance, for fifteen minutes at 154° F.—slowly raising to 165–166° F.—the latter usually being the final mashing temperature. The peptonizing enzyme "peptase" is most active at about 100–120° F.; diastase at about 140–154°; over 170° the diastase becomes very weak.

Malt contains diastase in quantities sufficient to convert into maltose more starch than that which is stored up in the malt itself and American malts on an average possess a much greater diastatic strength than German malts, in fact, their power in this respect is so great that there is danger of carrying saccharification too far, if the mashing temperatures that are customary in Germany were retained. Hence, the principles of raw cereal brewing became the subject of closer study in this country.

Water. The amount of water to be employed in the production of 100 barrels of wort or about 100 barrels of beer, is approximately 135 barrels. Some of the water employed is left in the grains (about 20 barrels), some is evaporated in boiling (about 10 barrels), some is evaporated on the surface cooler (about 5 barrels).

With *grits* and *meal* use: For 100 lbs. of material in rice tub, 1 barrel of water; for 100 lbs. of corn, 30 lbs. of malt. Boil grits 75 minutes, meal 45 minutes.

While the mash machine is in operation, a slow stream of water should be forced continually through the underlet (pfaff) to keep openings clear; also directly after stopping machine after reaching mashing-off temperature.

Live Steam can be employed directly for heating the mash, if the water used for boiler feeding is of good or medium purity, i.e., if it does not impart to the steam any obnoxious substances. Care should also be taken in the selection of a proper boiler compound for the same reason. Instead of heating with live steam the mash tun may be provided with a steam jacket or coil. When the end temperature is reached, a sample of the mash should not show any starch by the iodine test.

Let the all-malt mash rest thirty minutes and the cereal mash forty-five minutes. If allowed to remain standing too long the grains will settle too firmly.

Tapping. Open the taps wide, one by one, for a few seconds, and close them again; the recoil of the liquor will rinse out underdough. Then open the taps gradually until a proper flow of wort is obtained. Pump the wort back into the mash tub as long as it runs turbid, which usually lasts eight to fifteen minutes. The wort should then flow quite bright.

Sparging. This process consists in sprinkling hot water over the grains to wash out as much as possible of the valuable constituents remain-

ing in them. The amount of sparging water should be considered when starting the mash, with reference to the total amount of wort desired.

Boiling the Wort. The wort obtained by mashing is boiled for a certain period for the purpose of eliminating or rendering harmless certain undesirable constituents, like coagulable albuminoids, and introducing other new bodies, like hop resin and hop oil, by extraction from the hops. Besides, during heating and boiling the wort assumes a darker shade, due to caramelization of the sugars; water evaporates, resulting in a denser liquid, and the tannic acid of the hops coagulates an additional quantity of undesirable albumen, this coagulation aiding in clarifying the wort and causing it to " break."

In the United States the wort is generally heated by steam jackets and sometimes by steam coils, direct fire kettles having gone quite out of use. Steam is turned on when the wort flowing from the mash tub covers the heating surface in the copper, and the temperature kept at about 190° F. (70° R.) until all the wort, including spargings, has run in. Unless very pale beer is desired, the brewer may bring the wort to a boil while it is flowing in. During the boiling period the wort should be kept in a state of vigorous ebullition.

FIG. 317.—Brew-kettle.

Straining. From the copper, the wort runs into the hop-jack, where it is allowed to stand for a period, to permit the hops and albuminoids to settle.

The wort should not be allowed to rest longer than fifteen minutes, as a dark color or rank, bitter taste may result if wort is left in contact with hops too long. The hop jack is provided with a false bottom, through which the wort is drained into a pump that delivers it to the coolers. The hops remaining on the false bottom are sparged with hot water to wash out the wort they contain. If the wort remains in hop-jack very long, or if the spent hops are pressed out to gain the wort, a rank bitter taste of the beer is apt to result.

Cooling. The wort reaches the *surface cooler*, a large, shallow iron pan, and remains here a short period for the purpose of preliminary cool-

ing. The wort should be cooled to 145° F., and not lower, on the surface cooler, and receive proper aeration during cooling, avoiding all sources of contamination in the meantime. Aeration of the wort during cooling has the effect of further precipitating undesirable albuminoids. Besides, the wort absorbs air, which is utilized by the yeast later on. Most of the microbes that reach the wort below 145° F., will remain alive, the most common ones being butyric and lactic acid ferments and wild yeasts.

Baudelot Cooler. After the preliminary cooling the wort is sent over the Baudelot cooler, where it should be cooled down to 48° F., which is sufficiently low. Formerly it was a general rule, however, to cool the wort to as low a temperature as 42° F. The Baudelot cooler is a pipe cooler, in two sections, the upper one cooled by water, the lower one by brine or ammonia. The wort runs down over the outside surfaces of the pipes.

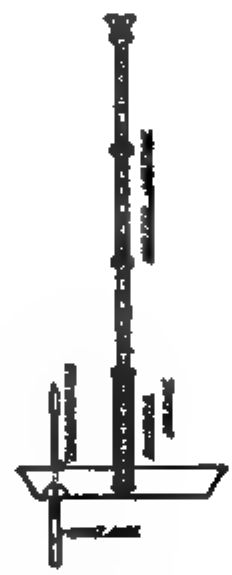

FIG. 318.—Baudelot Cooler.

Enclosed Cooler. These have been taking the place of the former in many breweries of late. The wort circulates through a pipe system and is cooled through a counter current of water until it reaches the brine or ammonia section. Artificial aeration must be provided.

Cold Break. After the wort leaves the coolers it should show a good "cold break," that is, it should settle clear in the sample glass at a temperature below 40° F., or filter clear. If it does not, the turbidity may be due to unconverted starch, to albumen, or to infection.

Loss in Volume. A certain loss in volume will occur on the passage of the wort from kettle to settling tank, due to (1) concentration in cooling, about $4\frac{1}{4}$ per cent; (2) evaporation of water, about 5 per cent; (3) adhesion of liquid to surfaces of vessels, pipes, etc., about $\frac{1}{2}$ per cent. When hops are properly sparged it will take about 107 barrels of wort in the kettle to obtain 100 barrels in the cellar.

Fermenting Cellar Operations. *Pitching with yeast.* Fermentation is induced in the wort by adding yeast properly prepared, which operation is termed "pitching." The common practice is to mix the yeast with

an equal quantity of finished wort or *first boiled* wort of about 55–60° F., rouse well to insure aeration and breaking up of cell aggregations, transfer to settling tank when the mass is in fermentation, mixing with it the wort as the latter runs from the cooler.

Amount of Yeast. The amount of yeast needed to secure a normal fermentation is from $\frac{3}{4}$ to $1\frac{1}{2}$ lbs. per barrel; the lesser quantities sufficing with lesser densities of wort, greater yeast vigor, better aeration.

Fermentation Phenomena. Within fifteen to twenty-four hours, according to the pitching temperature, little white bubbles appear around the sides of the vessel. The beer at this time is covered with a dark head of a thick consistency, composed largely of albuminoid matter, coagulated during the boiling period (sludge). The head of impurities being skimmed off, the whole surface is found to become quickly covered with a fine white froth (" whitening over "), rather higher around the rim than in the middle, denoting that carbonic acid gas is escaping through the fermentation of the sugar (maltose).

Kraeusen. The head of froth begins to move from the sides of the vessel to the middle, and assume a frizzled appearance, small cockle-shaped mounds beginning to rise all over the surface. At the expiration of twenty to thirty-six hours after pitching, the surface should be curly and pure white. (" young kraeusen "). From the time the froth head begins to move toward the middle, fermentation becomes more active, the head rising all the time (" high kraeusen "). At the same time the temperature rises, slowly at first, more rapidly as the activity of fermentation increases, while the saccharometer indication or density decreases more rapidly, the drop amounting to one-fourth to one-half of one per cent a day in the early part, and reaching one to one and one-half toward the high kraeusen stage. The curly head of froth turns a darker color while rising in height.

The high kraeusen stage is reached seventy to eighty hours after pitching and is maintained for a period of forty-eight to seventy-two hours, varying according to different influences. During this time the fermenting beer is kept at a certain low temperature, 48 to 50° F., and as high as 58° F., by means of attemperators, and when the head begins to collapse is cooled slowly to 39° F. The saccharometer falls more slowly as the end of the principal fermentation draws near. When the end is reached, the fall of the saccharometer is commonly $\frac{1}{10}$ to $\frac{1}{30}$ per cent in twenty-four hours.

The yeast, which had been kept in suspension during fermentation through the escape of carbonic acid gas, should now be found settled on the bottom of the fermenter; the amount being about three to four times the quantity used for pitching.

Sample Glass. In a sample glass the beer should show quick sedimentation and clarification in about twenty-four hours at cellar temperature.

Yeast Properties. Yeast has a thick, stiff pasty consistency, not watery or slimy, a yellow to brownish color, a bitter taste due to hop-resin, and a characteristic odor.

It consists, for the most part, of single cell organisms of the class saccharomyces and species cerevisiæ. Yeast mechanically encloses a large amount of water or beer—about 50 per cent—through which are dispersed minute bubbles of carbonic acid gas, that escape when the yeast is stirred, emitting a rustling sound. After the beer has run from the fermenter, the yeast sediment should be quite firm and thick. However, unless an absolutely pure culture, every yeast has an admixture of foreign organisms, as bacteria, wild yeasts, and mycoderma. All these impurities may be classified as "potentially dangerous."

Yeast Type. The course of the fermentation as performed by the yeast depends not only on the vitality and environment of the yeast, as age of yeast, temperature, aeration, composition of nutritive medium, presence or absence of other organisms, but also upon the type of yeast employed, which may be distinguished by differences in properties possessed, or effects produced by them.

Types of cultivated yeast are distinguished by differences in the following properties possessed, or effects produced, by them:

1. Degree of attenuation;
2. Fermentative energy, or rapidity of attenuation;
3. Reproductive energy, or growth of yeast;
4. Rapidity of settling of yeast, or clarification of beer;
5. Compactness of settling of yeast;
6. Qualities of beer obtained, as taste, odor, and durability.

Yeast Clusters. The grouping together in clusters of micro-organisms like yeast, is brought about by a mucilaginous secretion of the cell membrane, so that cells which come in contact stick together in larger or smaller cell aggregations or clusters or flakes. This gives rise to a more rapid settling of the yeast, that is clarification, after principal fermentation on storage and in chip cask, and more compact settling of the yeast in fermenting vat and yeast vat, a better break of the beer, and is of influence regarding attenuation. Low attenuating types form larger clusters than high attenuating types, while wild or foreign yeasts do not have the faculty to any extent.

Stock Cellar Operations. *Tanking the Beer.* The beer is brought from the fermenting vat to the stock tank either at the temperature to which it has been cooled in the fermenter and then it undergoes a secondary fermentation, or it is further chilled on its way to the stock cellar, passing it through a cooler in which case no secondary fermentation is anticipated and the beer should reach the stock tank thoroughly fermented.

Storage is that stage in which the beer is kept after the conclusion of the primary fermentation and prior to final clarification for the trade package.

The objects of resting the beer are to eliminate certain suspended matter, like yeast, thereby securing greater clearness, and certain objectionable matters, like albumins, thereby securing greater durability, especially in pasteurized bottled goods.

During the storage period there should be a slight progress of secondary or after-fermentation, unless final attenuation was reached previously. The residue of maltose and part of the maltodextrin are fermented by slow degrees, the amounts of carbonic acid and alcohol increasing.

The yeast settles the more quickly, the less sugar there is present and the smaller the storage vats; the albumins are the more thoroughly eliminated, the better the mash was peptonized, the lower the storage temperature, and the longer the period of storage. Hence, long storage at low temperatures enhances the stability of beer after pasteurization.

Starch particles do not settle on storage. Nor can dependence be placed on improving the beer through long storage in respect to number of bacteria it contains. On the contrary, bacteria may increase during storage.

Low temperatures while the beer is in storage, are necessary to precipitate the albumins and to check the development of bacteria. The storage cellar should be kept as near to the freezing point as possible.

Chip Cellar Operations. When sufficiently matured in storage, the beer is run or pumped into chip casks, so called from a method of clarifying beer by means of chips (which see).

Treatment in the chip cellar has a two-fold object:

1. To impart to the beer the necessary life, that is, a sufficient amount of carbonic acid gas so that it will foam properly when tapped. This is done:
   a. by kraeusening and bunging, or
   b. by charging with carbonic acid gas directly (carbonating), or
   c. by both kraeusening and carbonating.
2. To make the beer brilliant. This is done:
   a. by the addition of chips;
   b. by the addition of isinglass;
   c. by filtration.

Kraeusening. This consists in the addition of kraeusen beer, that is, young beer in the first, or kraeusen stage of fermentation, twenty-four to forty-four hours after pitching, the amount being about 15 per cent for home draught beer; 10 per cent for export draught or bottle beer, or 5 per cent when beer is carbonated. A few days after the kraeusen have been added the finings are introduced and the cask is bunged, to prevent the escape of the gas generated by the kraeusen, its accumulation causing a pressure which is termed *bunging pressure* and which is allowed to rise to about 5 lbs.

Carbonating. Carbonic acid fermentation gas may be introduced into the beer at any stage after fermentation, but usually this is done

while the beer is being transferred from the chip cask to the racking bench and before it reaches the filter. When beers are carbonated they are either not kraeusened at all or only with relatively small quantities of kraeusen; about 5 or 6 per cent. The gas is introduced either on the *pressure* principle by spraying the beer through a compressed atmosphere of gas or on the *aspirator* or *injector* principle, by forcing the gas into the beer, usually in a conduit while in motion.

Clarification. Matter remaining in suspension at the end of the storage period is eliminated by mechanical means. First among them is the introduction of chips. *Beer chips* or *clarifying chips* are pieces of wood, usually of beech or maple, so cut as to present a maximum of surface with a minimum of volume and weight. The chips are spread in the bottom of the chip cask, where they retain particles in suspension, reaching them as well as the sedimentation caused by the employment of isinglass. Chips must be carefully prepared by boiling in water, with an addition of soda.

Fining the Beer. Brewers' finings are prepared from so-called *isinglass*, obtained either from *fish* through cleaning, rolling and drying the bladder, or from *hide* of *calf*. The finings may be prepared on the cold or warm plan, their efficiency depending upon the amount of gelatinous substance the isinglass yields and which in flocculent form distributes through the beer enveloping the suspended particles and carrying them to the bottom. One pound of isinglass is sufficient for one hundred to five hundred barrels of beer.

Filtration. The process of filtering beer consists in forcing the beer on its way from the chip-cask to racking apparatus, generally by means of air pressure applied at the chip cask, or through a pressure regulator pump interpolated between chip cask and filter, through one or more layers of compressed fibrous material, called filter mass, which commonly consists of wood pulp or paper pulp. Beer should always pass through the filter under back pressure, as it will otherwise foam to such an extent as to preclude the proper filling of the trade packages. It should stand in a cold place, if practicable, in the chip cellar.

Back-pressure Racking. The principle of back-pressure racking is to create in the delivery package a back pressure sufficiently high to prevent foaming of the beer, so as to permit of readily filling the package without loss of time and without the foaming and loss of beer accompanying the practice of " gut racking " which formerly obtained.

Special Brewing Systems. The practice of storing the beer for a long period in cold cellars is a rule with some exceptions. Different systems have been installed to obviate this necessity, the principle being to obtain complete or final attenuation in the fermenting vats. Such systems are:

Pfaudler System. Employing glass enameled steel tanks throughout and vacuum and aeration for completing fermentation; finishing the

beer by kraeusening; *Schneible system*, with high fermentation temperatures; chilling and carbonating beer from fermenter to finishing tank; *Selg system*, giving attention mainly to yeast culture, the constructive copper or steel fermenting vat with conical bottom permitting removal of sedimentation at any time; *Nathan system*, only tried experimentally in Europe, aiming at cooling of hopped wort, aeration, fermentation, chilling, carbonating and finishing—all in one tank.[1]

English Top Fermentation Beers. The beers brewed in the United Kingdom and its possessions show similar characteristic differences in their properties as the German beers. They are called *ale*, *porter* and *stout*.

Mild beers, whether ale, porter or stout, are such as undergo no secondary fermentation, but are marketed about seven days after the principal fermentation is finished.

Stock beers, or *old beers*, whether ale or stout, are such as have undergone a secondary fermentation and are stored about two months or more before marketing.

The mild beers are distinguished from the stock beers by a more sweetish (mild) taste, containing more unfermented malto-dextrin and less acid, the old beers, on the other hand, becoming more alcoholic and tart. There is, therefore, much difference in the properties of mild beers and old or stock beers.

Mild ales, are usually brewed of a darker color than old ales, with less original gravity and less hops.

Old or *stock ales* have a pale to amber color, quite bitter and more or less tart taste, strong hop flavor, and though brewed with a high percentage of extract, have less extract left, but contain more alcohol than stout, which is mainly due to the practice of dry-hopping ales, which results in breaking down the malto-dextrins more effectually than is the case with stout, which is not dry hopped.

Stouts are quite dark, almost black, have a pronounced malt-caramel taste and aroma, a sweetish taste if mild, and a more or less tart taste, according to age and circumstances. They are brewed stronger than ales.

Porter is brewed less strong than the old beers. It stands in a similar relation to stout as does a mild ale to a stock ale.

Brewing Materials in England. The materials used in England, besides malt, hops and water, are usually sugars of different kinds. Such are caramel (produced from glucose) for black beers, invert sugar and glucose for mild and stock ales, while of late years, rice, maize and wheat are gaining in favor. The English drinking public now prefer beers of low gravity to the stock beers, and since they should contain only a moderate amount of alcohol, but sufficient extract to be full to the palate, sugars should be used for these beers, containing the requisite amount of unfermentable extract.

[1] For American Pasteurized Bottle Beer, see Bottling Plant, succeeding Brewing Equipment.

Malt. Most brewers use some foreign barley malt, together with that produced from domestic grain, on account of the better clarification of beer and better drainage of wort, while some brewers use California barley malt entirely, the beer from which keeps better in hot weather. Usually pale malt is employed in the production of all the beers, together with some coloring material, preferably caramel, brown malt, amber malt or roasted corn for dark ales, porter and stout. Sometimes black beers and mild ales receive an addition of caramel solution in the fermenting vessel just prior to the close of the principal fermentation. For dark beers higher kiln-dried malts are preferred by many brewers.

Hops. With regard to hops, the English brewer favors the employment of foreign qualities of hops to blend with the domestic article, the proportion frequently rising to 50 per cent, chiefly American hops or "Yankees." The English hops are distinguished for their delicacy of flavor, especially the East Kent goldings, and these are eagerly sought for flavoring choice pale ales in dry hopping. The relative quantities of hops and of other materials to be used in brewing the different beers, according to the gravity of wort and other requirements, may be gathered from the introductory remarks in the paragraph on "Brewing" also salient differences in regard to the brewing process employed for the different types of beers.

Brewing Operations for English Beer. The method of mashing is essentially the same for ales and stouts whether of the "stock" or "mild" type. The crushed malt is passed through a "pony masher," where it strikes and is mixed with the mashing water of about 165° F. for ales, and slightly lower for stouts, the initial or mashing temperature being about 150° F. for the former and 145° F. for the latter. After thorough mixing in the mash-tun the temperature is brought up, by underflow of hot water, to 154°, the stirrer is stopped, and the taps are opened after about two hours. The grains are sparged with water of about 170 to 160°. The wort flowing into the kettle is kept heated to near boiling-point until full, when hops are added ($1\frac{1}{2}$ to 3 lbs.) and boiling (simmering) continued from one to two hours, when it is "turned out" into hop-box, strained, pumped on surface cooler, then run over pipe cooler, and yeasted at 58 to 60° F.

Top-fermentation Appliances and Operations. The essential difference between top fermentation and bottom fermentation is in the behavior of the yeast, which rises to the top during top fermentation, where it is either removed by suitable implements, by a process called "skimming," or it is allowed to work out of an aperture at the top of the fermenting vessel, by a process called "cleansing." If the cleansing takes place in casks, the yeast working out through "swan necks" into a common trough, it is called "Burton union system"; if through openings (lips) in the top and edge of upright tanks, the tanks themselves being so placed as to form a trough for the yeast, it is called "Ponto system." Then there is a com-

bination of the skimming and the cleansing systems in the "stone square system," the yeast working out through the top of a closed stone square, from where it is removed by skimming.

Secondary Fermentation. Most English beers are sent out directly after racking, dry hopping and fining, without going through any secondary fermentation. Stock beers, however, undergo a secondary or slow fermentation in the storage or trade cask. The malto-dextrins of the beer supply the substance for this fermentation, being partly degraded by inversion enzymes contained in the yeasts and by the diastase introduced in dry hopping. Thus, beers that are dry hopped ferment down lower in the cask than beers unhopped in cask, like most black beers. The fermentation of the sugars, formed by the breaking down of the dextrins, keeps the beer charged with carbonic acid gas, and this condition is essential for checking the development of foreign ferments. Therefore, a sound secondary fermentation is of the greatest importance.

Dry Hopping. Ales usually, and black beers sometimes, receive an addition of hops in the storage or trade cask, the quantity varying from ¼ lb. for mild ales to 1 lb. per barrel for pale, bitter and stock ales.

Priming. Often a solution of some kind of sugar is added to the beers, especially the black beers, in the cask, which process is called priming. The object is to impart sweetness or body, or to aid secondary fermentation and give "life" or what in England is termed "condition" or "briskness."

Vatting. In many breweries it is still customary to blend a young beer with an old one that shows acidity and proper flavor in a marked degree, in order to give the product the character of age. Especially is this done with stouts. The old beers are called vats, and as much as 25 per cent is blended at times with the young beer.

Bottling Ales. Ale for bottling should be (according to Wright) allowed to go through all its cask changes, spontaneous brilliancy (unaided by finings) at the end of them being the simplest criterion for bottling.

American Ales. In the United States a somewhat different system of brewing has developed in the production of top-fermentation beers, from those employed in England. While the American stock beers are patterned after the English stock ales and stout, *cream, lively,* or *present use ale* takes the place of the English mild ales, and more recently the American ale brewers have equipped their plants with refrigerating machines to brew a beer—*brilliant* or *sparkling* ale—that combines the properties of lager beer and ale, i.e., a sparkling, brilliant beer with an ale taste and aroma. Since these ales have been put on the market, top-fermented beers have gained some of the ground which they had lost in competition with lager beers.

In the main, the equipment of a modern American ale and porter brewery does not differ essentially from that of a lager beer brewery. The chip-cask cellar of the lager beer brewery, however, can be dispensed

with, a carbonating room taking its place, while the stock cellar is retained, since some of the ales are stored.

Berliner Weiss Beer. Of the many varieties of top-fermentation German beers, it is only *weiss beer* that has been able to compete with the lager beers, while the others, being gradually displaced, are but little known, or enjoy only a local reputation.

Berliner weiss beer should have a very pale color; be moderately clear, distinctly tart, rich in carbonic acid, so that it foams strongly when poured, and should hold the foam moderately well. The difference in the production of weiss beer and the other beers described consists in the materials employed, which is generally one-third barley malt and two-thirds wheat malt; in the gravity of the wort, which is usually below 10 per cent; in the quantity of hops used, usually less than ½ lb. per barrel; in the fermentation, during which lactic acid bacteria are allowed to develop, the weiss beer yeast containing these in large numbers, and in the treatment after fermentation, the weiss beer not being stored but mixed with fermenting beer, which mixture being filled into bottles—where fermentation continues—results in a large quantity of carbonic acid gas being retained in the bottles, and gives to the finished product the characteristic life. The large amounts of lactic acid bacteria do not permit of clarification of the product, whereas ales and stouts are usually clear and lager beer usually brilliant.

Lager Beers in Germany and Austria. Besides the recognized types, like the *Bohemian*, *Vienna* and *Bavarian* beers, of each of which there are brewed two varieties, the *Schenk* or *winter beer*, and the *lager* or *summer* beer, there are brewed for special purposes beers of each type like *Bohemian export*, *Vienna export* or *Bavarian export*, or beers brewed for special occasions, like *bock*.

Bavarian Beer is light brown (like the Munich) to dark brown (like the Kulmbacher). It has palatefulness, a sweetish taste and malt flavor, moderately attenuated through fermentation (65 to 70 per cent) original gravity of wort 12½ to 15; for bock and export 15 to 18.

Bohemian Beer (like the Pilsener) is light yellow to greenish yellow, the taste is vinous, dry, somewhat sharp, bitter taste of hops predominates. More strongly attenuated than Bavarian, 70 to 75 per cent. Schenk beers brewed 10½ to 11½; lager and export 12½ to 13.

Wiener Beer is less bitter and darker in color than Bohemian and has less malt aroma and is paler than Bavarian. In all respects it takes a medium position between both. Schenk beer about 11; export or "Maerzen" about 14½ to 15.

Kulmbacher. A very dark beer with the Bavarian characteristics especially accentuated, brewed along the lines of a Bavarian lager, from a very strong, original gravity of wort of about 18 to 19 per cent.

Dortmunder. Pale, like Bohemian, of about 14 to 15 per cent; from low dried malt; strongly hopped, highly attenuated.

Export and *Bock* differ from the Schenk and lager in that they are brewed stronger and contain more alcohol. Thus the percentage of alcohol and extract found, as the result of the analyses of a large number of beers, was on the average: [1]

	Alcohol.	Extract.
Schenk or winter beer	3.36	5.34
Lager or summer beer	3.93	5.79
Export beer	4.40	6.38
Bock, Doppel, or Maerzen	4.69	7.21

For general character of these beers refer to introductory remarks in the paragraph on "Brewing," also for materials employed and brewing processes.

The *mashing method* is peculiar inasmuch as three parts of the whole mash, called the first, second and third mash, are successively boiled each for ten to forty-five minutes, and returned to the mash tun. In Bohemia, where pale beers are the vogue, boiling is often restricted to ten, fifteen or twenty minutes, in Vienna generally thirty minutes, in Bavaria often forty-five minutes. By returning the boiled portions the mash is successively heated from 95° F., the initial temperature, to about 122°; then to 145° and finally to about 160°.

After inversion is completed, the mash is run into the strainer. The subsequent operations of straining, fermenting, sparging, boiling, hopping, cooling, fermenting, storing, are carried out much in the same way as in the United States. There is, however, no separate chip-cask treatment, with its processes of fining, kraeusening or carbonating. After the beers are stored for some time, usually for six weeks or two months, chips are introduced into the storage cask and the beer is bunged, the secondary fermentation being depended upon to furnish the requisite life.

Malting is the process of preparing cereals, usually barley, for brewing purposes.

Barley is the favorite cereal employed, chiefly because the husk acts as an excellent filtering material in the mash tun; its endosperm is readily modified and mellowed during growth, unlike corn; and it develops a sufficiency of enzymes during the malting process.

Oats, the only other cereal which retains its husk in threshing, contains large quantities of objectionable albumen, that preclude its employment.

In the United States, the systematic study of American barleys, with a view to their improvement, was begun in 1904 by the United States Department of Agriculture, and was fruitful of much new knowledge.[2]

The history of barley culture in the Western States of the Union may be

[1] "American Handy Book of the Brewing, Malting, and Auxiliary Trades," 1908, p. 1250.

[2] U. S. Dept. of Agriculture, Bulletin No. 124, Bureau of Chemistry, on "Study of American Barleys," by Leclerc and Wahl.

dated from the settlement of German pioneers in the territory which is now the State of Ohio. In the Eastern States only local or Canadian barley was used up to about 1875, when the Manchuria barley, introduced into Wisconsin from Germany (about 1880), and thence spreading into Minnesota, Iowa, South and North Dakota, became the dominant

FIG. 319.—Barley Types: to the left, six-rowed (Utah Winter); in the middle, Two-rowed (Chevalier); to the right, six-rowed Drooping (Manchuria) or common.

type on the American market. The Bay Brewing type is mostly cultivated on the Pacific Coast in California, Oregon and Washington; the White Club in Utah, Oregon and Washington; the Chevalier or two-rowed type, in Montana, California and the British Northwest.

The *barleycorn* consists in the main of the *husk*, the *germ* and the *endosperm*. The husk is mainly for protection, the germ contains the

vital principle endowed with the faculty of growth, under suitable conditions, into the new plant, and the endosperm contains the bulk of the nourishment to sustain the germ until, in the natural order of things, the green leaves are sufficiently developed to assimilate carbonic acid from the air.

Through *germinating*, the endosperm of the barley is modified, thus becoming more porous as particles of starch, albumen and phosphates are made soluble by the action of diastase, peptase and lactic acid, and utilized by the germ, as food in the form of amides, sugar and acid phosphates, while caramel is formed on the kiln in proportion to moisture contained at high temperatures.

During growth the germ of the barleycorn develops the *acrospire* or *plumula*, and the *radicle*. The former is that part from which develops the green blade which appears above the ground where barley is planted and eventually produces the stalk. The radicle sends out a number of shoots that develop into the roots of the plant and are commonly called *rootlets*.

In germination, the rootlets protrude at the germ end of the grain, while the acrospire, starting from the same end, grows up toward the other end of the grain, keeping under the husk along the back or solid side of the grain.

In malting, it is not allowed to reach the point of breaking out, the growth being checked suddenly by kiln-drying before the acrospire quite reaches the opposite end, experience having demonstrated that the most desirable condition of the endosperm coincides with that degree of development of the acrospire. For properties of malt, see "Brewing Materials."

Malting Operations. Broadly these embrace every manipulation from the moment the crude grain leaves the elevator or storehouse up to the time the finished malt is conveyed to the storage bin or to the hopper to be measured into the crusher mill of the brewery. In a more confined sense, as treated here, the term is applied only to the three main operations of steeping, germination and kiln-drying.

Growth. Germination as conducted on a smooth floor constructed of cement for this purpose, is the traditional method, the process being called "flooring," "growing," or "germinating." The modern methods, however, are based on artificial or forced aeration (pneumatic malting) either on a perforated floor or in revolving drums. Another important distinction is, that by the old method the work is almost entirely done by hand, whereas the improved methods may with much propriety be called mechanical malting, most of the work being done by machinery.

Floor Malting. The barley from the bins is loaded on the conveyor and carried automatically to the cleaning machine. The offal goes to feed dealers.

Steeping. From the cleaning machine the barley drops into the separator underneath. The different grades, two or three in number,

go to the automatic scales, and then reach the steeping tank, which should be half filled with water. At first, the water should stand 1 to 2 ft. above the barley when the tank is full. The skimmings are floated off or skimmed off with a ladle. They go to a separate bin or trough, and are dried and sold for feed. Change the water twice the first day and once a day thereafter. Steep for about forty-eight hours, modifying for dryness of air, hardness and temperature of water, type and condition of barley, etc.

Germinating. The grain being fully steeped, the water is drained off at the bottom and the barley dropped on the malting floor; other-

FIG. 320.—Floor Malting with Power Shovel and Bucket Elevator.

wise it is loaded on trucks and wheeled to the floor where the grain is spread and leveled to a heap or "couch" of about 8 to 10 ins. Here it is turned from time to time by hand shovels and its height gradually increased and again reduced according to conditions from about 14 ins. to 4 or 5 ins. The temperatures in the air should be about 50 to 60° F., in the growing malt couch about 75°, turning to prevent too high heats and to supply aeration. Growth takes about five days for barley of the Manchuria type and eight days for Bay Brewing and two-rowed types, like the Chevalier. When the endosperm has become mellow and the acrospire is three-quarters up, the "green malt" is conveyed to the kiln which

usually has two or three floors heated by open fire assisted by closed heaters; hard coal being smokeless, is commonly used for fuel.

Kilning. By a fan installed above the upper floor air is sucked through the malt together with the products of coal combustion. The temperature is kept at about 90° F. on the upper floor, and when hand dry, usually after twenty-four hours, the malt is dumped on the lower floor where it is kept for about twelve hours at 120–130° F., where it is kept practically dry, when it is heated to the final temperature of 150–155° F., for pale beers; 165–180° for darker beer and up to 220° F. for beers of Munich character.

forated cylinder in which a shaft with helically arranged arms is revolving thereby carrying the stems toward one end and causing the berries to fall through the perforations.

The machine in which the grapes are crushed usually consists of a hopper feeding the grapes to a pair of adjustable grooved rollers revolving in opposite directions and with unequal speed. The purpose is to thoroughly open up all of the berries without crushing the seeds from which undesirable substances would otherwise be extracted, whence the rollers are adjusted accordingly. Part of the must is often allowed to drain off from the crushed grapes by gravity alone and may be fermented separately as being superior to the rest of the must that is obtained by pressing.

The wine presses are mostly ordinary screw-presses, sometimes however hydraulic presses are used. The crushed grapes are spread in a uniform layer over the press-bed and subjected to a gradually increasing pressure. Too strong pressure should not be applied at once lest the yield be diminished. As already stated the pressing of white wines takes place before, that of red wines after fermentation.

The Must. The grape juice is a watery solution, the main constituents of which are:

1. Sugar;	4. Flavoring substances;
2. Organic acids;	5. Pectine and mucilaginous substances;
3. Albuminoids;	6. Mineral substances.

1. The sugar, during fermentation, is split up into about equal parts of alcohol and carbonic acid, and only very little sugar (less than 0.15 per cent) should be left in ordinary dry wines. A must containing 16 to 17 per cent sugar will produce a table wine with an alcoholic strength of 8 to 8.5 per cent by weight; musts containing less sugar produce the light ordinary wines, those containing more sugar result in the heavier high-grade wines.

2. The organic acids, tartaric and malic, although present in comparatively small quantities are very essential constituents of the must. The tartaric acid mainly occurs in combination with potassium as tartrate (bitartrate of potassium) which is precipitated to a large extent during the fermentation. A part of the acids is also consumed by the yeast and by certain bacteria which accounts for the fact that a wine has less acidity than the corresponding must. The total acidity of must or wine is usually given as the apparent percentage of free tartaric acid.

To make a wine palatable its acidity must be in proper ratio to its alcoholic strength and palatefulness. A light wine without prominent flavor and body may appear fully harmonious as to taste with an acidity of only 0.4 per cent, but a heavier, highly flavored, wine would taste quite flat when possessed of this same acidity and may require as much as 1.0 per cent acidity to appear harmonious.

A must usually looses from 0.2 to 0.6 per cent in acidity during its transformation into wine.

3. The must can contain up to about 1 per cent of albuminoids of which only approximately one-half remains in the wine, the rest being utilized, partly as nourishment by the yeast, and partly precipitated during the fermentation.

4. The flavoring substances of the must upon which its quality largely depends are present in too small quantity to be determinable by chemical analysis and we possess at the present time only scant knowledge of their chemical nature.

These flavoring substances increase during fermentation, the fermented must containing: 1. Those originally present in the must, 2. Others formed during the fermentation, probably mainly by decomposition of certain albuminoids (amino-acids) contained in the must, and 3. The specific flavoring substances produced by the different varieties of yeast irrespective of composition of the must. 4. The pectine and mucilaginous substances causing the thick consistency of the must are practically all precipitated during the fermentation as they are insoluble in dilute alcohol. 5. In a normal must is found from 0.3 to 0.5 per cent of mineral substances (ash) the amount of which considerably decreases during the fermentation owing to the precipitation of potassium in the form of tartar.

The wine maker tests his must to determine approximately the sugar and acidity of an average sample. The sugar is determined by means of areometers such as Oechsle's must scale, indicating how many grams one liter of must weighs more than one liter of water, or Balling's saccharometer indicating the percentage of solids in solution. Degrees Oechsle divided by five, or per cent Balling multiplied by $\frac{5}{6}$ gives the sugar content in per cent of an ordinary must with sufficient accuracy for practical purposes. The acidity is measured by titration with standardized alkaline solutions. Knowing the ratio of sugar to acidity the wine maker is in a position to carry out the subsequent operations with a view to either checking or facilitating the decrease in acidity according to the requirements.

A direct correction as to composition may also be found desirable. If lacking in acidity the must can be corrected by the admixture of less ripe grapes or by the addition of tartaric acid. The addition of gypsum, which is sometimes used, especially in making red wines, has a similar effect, the gypsum reacting upon the tartar so as to form insoluble calcium tartrate and bisulphate of potassium which latter substance, unlike the tartar, remains dissolved in the wine. This method, the so-called plastering, can only be used to a limited extent, since the laws of most wine producing countries fix a maximum limit for sulphates contained in unadulterated wine.

If the must is too rich in acids, the acidity can be reduced by dilution with water and the proper sugar content eventually restored by addition of pure cane or grape sugar. This process, known as gallizing is used to

some extent in northern countries especially for white wines and is generally considered legitimate, provided it is carried out so as to actually improve, or to render marketable, the product and not with a view to unduly increase its quantity.

The Fermentation. When left to itself the must will soon begin fermenting. It grows quite turbid, gas bubbles rise to the surface, the temperature rises and the viscosity and specific gravity decrease. At the same time the sweet taste gradually changes into a vinous one and a distinct flavor develops. Toward the end of the fermentation the turbidity gradually disappears and the completed fermentation leaves the young wine in a limped state on top of a heavy sediment.

These changes are brought about by certain microscopical plants that are always present on the skins of ripe grapes. Among them the yeasts which cause the alcoholic fermentation, splitting up sugar into alcohol and carbonic acid, are desirable and indispensable, while others such as mycoderma and various bacteria are undesirable disease germs.

Between the microorganisms a struggle for life goes on in the must, each one striving to utilize the nourishment on hand for its own growth and pr.ducing substances that are injurious to its competitors. By far the most important task of the wine maker is to assist the yeast in this struggle by offering it the most favorable conditions for its activity. His aim is to make the yeast ferment the sugar as completely as possible which not only means little nourishment left for other organisms but also a high percentage of alcohol prohibiting their growth. Incomplete fermentation on the other hand results in a weak and unstable wine subject to a variety of undesirable changes.

The Wine-yeasts. The alcoholic fermentation of the must is caused by small, usually unicellular budding fungi, mostly belonging to the different varieties of saccharomyces ellipsoideus. Their principal breeding places in nature are the ripe juicy fruits where they multiply abundantly during the fall. Some of them penetrate with the rain to a certain depth into the soil, where a sufficient number keep alive over winter to repopulate the fruits of the following year, to which they are carried by insects, rain-splashes or the wind. Their perpetuation is facilitated by their power of forming spores, small resistant cells appearing under certain conditions within the vegetative cells.

The yeast cells contain an enzyme, the zymase, which in contact with dissolved sugar transforms it into alcohol and carbonic acid. This fermentation proceeds most satisfactorily at medium temperatures, the yeast becoming temporarily inactive at a few degrees above the freezing point of the water and permanently weakened at about 100° F. Even the most vigorous yeast can only produce about 13 per cent of alcohol by weight and this only under exceptionally favorable conditions.

Besides the main products of the alcoholic fermentation smaller quantities of glycerol, succinic acid and fusel oils are also produced by the

yeast during fermentation. Apart from the glycerol, that may—as far as our present knowledge goes—be derived from the sugar, the other by-products have recently been shown to originate from amino-acids (e.g. succinic acid from glutamic acid and amyl-alcohol from leucine) the nitrogen being utilized by the yeast in the form of ammonia for building up the albumen of its own body. In all probability flavoring substances are formed by a similar process from other amino-acids, the primary products being various alcohols and acids, which during the ripening of the wine are further transformed through oxidation and esterification.

Pure Cultures of Yeast. After the Danish scientist Emil Christian Hansen about twenty-five years ago, had discovered means of distinguishing between the different varieties of saccharomyces and had shown the great advantage of using pure cultures, derived from one single cell, in the brewing industry, many different wine-yeasts have been isolated and studied. They were found to differ, more or less, not only morphologically but also as to the rapidity and completeness with which they ferment sugar, as well as to their power of decreasing the acidity and as to the strength and fineness of the flavor they produce. This naturally led to the use of selected pure cultures of yeast for the fermentation of wine. Such cultures are kept in stock and furnished by especially equipped laboratories. In the wineries they are first propagated in a suitable quantity of boiled and cooled must, which is allowed to come into vigorous fermentation before being added to the bulk of the ordinary must. The addition of only $\frac{1}{2}$ per cent suffices to secure the predominance of the selected yeast.

The use of selected pure yeast results in better control of the operations, a cleaner taste and flavor and an earlier ripening of the wine. A specific flavor is also to some extent obtained, according to the yeast variety employed, but many exaggerated claims have been made in this respect by too ardent advocates of the pure cultures. If wines are to be re-fermented pure cultures are particularly useful, and special advantages are also derived from their use in the manufacturing of sparkling wines.

Undesirable Microorganisms of the Must. Among the microorganisms occurring on the ripe grapes together with the genuine wine-yeasts the most important are: saccharomyces apiculatus, mycoderma vini, and acetic acid bacteria.

The small lemon-shaped cells of saccharomyces apiculatus are often present in sufficiently large numbers to start the alcoholic fermentation of the must, but they are soon superseded by the more vigorous saccharomyces ellipsoideus. They produce a less desirable flavor and one of the purposes in using pure cultures of yeast is to restrict their activity.

Mycoderma vini forms a film on the surface of the wine and consumes alcohol, transforming it into carbonic acid and water by oxidation. Though it may not be directly harmful, it thereby renders the wine less resistant against the attacks of other disease germs.

The acetic acid bacteria, minute rods that are often united in long

chains, produce acetic acid from alcohol and are, therefore, very dangerous disease germs. As little as 0.1 to 0.15 per cent of acetic acid makes a wine decidedly "pricked" and with a content of 0.25 per cent most dry wines may be considered undrinkable. Exclusion of the atmospheric air protects against the growth of these bacteria.

Other diseases (turbidity, unclean, bitter or sour taste, ropiness etc.) are occasionally caused by other bacteria, especially in the lighter grades of wine or in wines that have not been completely fermented.

White Wines. The white wines are produced by fermentation of grape juice that has been separated from the skins, seeds and stems. A fermentation of this kind offers comparatively little difficulty, but the resulting wine is decidedly more delicate than those fermented on the skins, whence its subsequent treatment and proper ripening require greater care.

The fermentation is usually carried on in casks that are filled to $\frac{7}{8}$–$\frac{9}{10}$ of their capacity with grape juice and the bung hole is closed so as to allow the carbonic acid to escape but no air to enter. The duration of the fermentation is from one to two weeks depending on the temperature, which usually is 60–70° F., and on the quantity of yeast originally present. At the end of the fermentation the yeast sediment is sometimes stirred up again in order to facilitate the complete splitting up of the sugar and the reduction of acidity.

After the fermentation is over the wine is drawn from the lees into another cask in which some sulphur has been burned to check the further activity of micro-organisms. This cask is completely filled, tightly bunged and as a rule kept at a temperature of 50–55° F. Before the rising temperature of the following spring causes a slight revival of the fermentation, the wine is racked off from the sediment once more, and this process repeated several times during the subsequent ripening period. At each racking an oxidation takes place resulting in precipitation of certain albuminoids and further development of the flavor, until finally the wine has become sufficiently stable to be filled into bottles.

In the ordinary grades of wine this ripening is generally more or less forced by means of a more thorough aeration during the racking, artificial clarification, (filtration or use of finings), and, eventually pasteurization.

The simplest form of wine filter is a cylindric or conical linen bag into which the wine is poured back until it runs clear. The more modern filters are closed so as to protect the wine from the air. Their filtering material is either pure cellulose or paper-pulp, packed into one or more filtering chambers or especially prepared asbestos-wool stirred up with a smaller part of the wine and pumped into the filter where it deposits as a uniform layer on walls formed of fine wire screens.

Finings are added to the wine in order to produce a very finely distributed sediment of higher specific gravity which will gradually settle to the bottom carrying with it all suspended solid particles. For fining

white wines isinglass is commonly used. It is soaked in water and at last in wine until nearly transparent and then vigorously beaten with some more wine eventually under addition of tartaric acid, filtered through linen and thoroughly distributed into the wine in the cask. One ounce of isinglass can generally fine 200–500 gallons of wine within 8–10 days.

Red Wines. The red wines derive their characteristics from being fermented in contact with the skins of red grapes, from which they extract not only coloring matter but also a variety of other substances, especially tannins. Normal red wines contain from 0.1 to 0.3 per cent of tannin while the percentage of this substance in white wine does not as a rule exceed 0.02 to 0.04 per cent. Owing to this high content of tannin the ripening of red wines is a comparatively easy matter once the fermentation has been properly carried through, but the presence of the skins at the fermentation on the other hand gives rise to several difficulties during this process.

The carbonic acid carries the skins to the surface where they form the so-called cap, which must he pushed down repeatedly in order to insure proper extraction and uniformity of fermentation. Closed casks are therefore less suitable and in the open tubs, which are generally used, there is great danger, however, of acetification owing to the free exposure of the cap to the air. To overcome these difficulties the fermenting tubs are often provided with removable grates that are held in horizontal position about 5 ins. below the surface of the liquid thus prohibiting the skins from rising to the surface. To insure proper uniformity the wine is drawn off at intervals from the bottom of the tubs and pumped back to the surface.

The temperature during fermentation of red wine is usually 65 to 85° F. As red wines are mainly produced in southern countries it is often difficult to prevent the temperature from rising too high, a considerable amount of heat being generated by the decomposition of the sugar. Too high temperature not only facilitates the growth of various bacteria but also prevents the yeast from completing the fermentation, the result being a wine of poor quality and easily subject to further deterioration. Artificial cooling is therefore often resorted to, water being circulated through cooling coils in the tubs or the wine being pumped through enclosed coolers.

After being fermented the red wine is drawn off into casks, which, however, are only sulphured in exceptional cases, because most red wines do not need this protection and would be more or less bleached by the sulphurous acid. Red wines are ripened in practically the same way as white wines but less time and fewer rackings are required to render them sufficiently stable for bottling.

The red wines are mostly fined with gelatine or white of egg. The gelatine is soaked in water over night, dissolved in wine by gentle heating, cooled, stirred up with some more wine and added to the cask. One ounce of gelatine is required for 50–120 gallons of wine. Whites of

eggs are often used to fine the better grades of red wine, one white for every 8–12 gallons. They are first beaten to a foam, pressed through a heavy linen, and then stirred up with some of the wine before being added to its bulk.

Sweet and Dessert Wines. The white and red wines referred to above are all dry, i.e., practically all of their sugar having been fermented. The sweet wines and the dessert wines on the other hand contain unfermented sugar besides a high or even very high percentage of alcohol. The typical sweet wines such as "Auslese" rhinewine, sauterne, or tokay contain much sugar but their alcohol is produced by fermentation and consequently does not exceed 13 per cent by weight. The dessert wines such as port, sherry, madeira and malaga are less sweet but generally oontain from 15 to 20 per cent by weight of alcohol part of which has been artifically added.

The " Auslese " wines and sauternes are produced from grapes attacked by a certain mold, botrytis cinerea, which finds favorable conditions for its growth in a foggy, cool climate without too much rain. It causes the grapes to shrink and to partly dry up; the must being accordingly more concentrated and possessed of a peculiarly fine flavor. The fermentation is carried out with a view to produce enough alcohol to prevent further changes, but since sugar is left unfermented these wines are prone to after fermentation and as a rule need heavy sulphuring to become stable.

In certain territories the dry and warm climate allows the grapes to dry up similar to raisins before they are picked. These yield a very concentrated must. The tokay wines of Hungary are made from such grapes, extracted with normally fermented dry wines and pressed. Imitated tokay is made in a similar way from ordinary dried raisins or from must concentrated by boiling in vacuo.

The various dessert wines contain more alcohol than can be produced by fermentation. An addition of alcohol is therefore necessary, and is often combined with an addition of condensed must or sugar. The alcohol may be added either at the end of the fermentation or at an earlier stage, in the latter case preventing part of the sugar contained in the must from being fermented. The addition is often made step by step, part of the total amount required being added at each racking and thoroughly mixed with the wine. During the ripening period the dessert wines are kept at a comparatively high temperature and freely aerated. This results in the development of the peculiar flavor known as madeira flavor.

Sparkling Wines. The sparkling wines are produced from either red or colorless grapes, the juice alone being fermented as usual for dry white wines. After being drawn off from the lees the wine is racked once more, a too high content of albuminoids being eventually decreased by an addition of tannin. The wine is blended in large vats or casks with a view to produce a uniform product from one year to another, and enough sugar solution is added so that a pressure of about 5 atmospheres

can develop during the subsequent fermentation in bottles. Furthermore a culture of selected pure yeast is often added and the wine is then bottled and corked, preferably in the spring because the rising temperature facilitates fermentation. When bottled the wine has a temperature of 65–72° F., but the bottles are kept at about 50° F., when the fermentation has started. This temperature must be kept as constant as possible to avoid breakage. The duration of the bottle fermentation varies from one-half to two years. When the proper pressure is reached the bottles are placed in a slanting position on special stands, their necks being a little lower than their bottoms. A short shaking and turning movement is imparted to them once a day during about six weeks while they are gradually raised to a vertical position neck down. In this way the yeast sediment is carried down on the cork leaving the wine entirely clear. This process can be greatly facilitated by the use of a proper variety of yeast; i.e., one combining a strong fermenting power with a tendency to grow in larger clusters.

The bottles are now taken to the uncorking room and eventually cooled to bind the carbonic acid more firmly. The uncorking requires a good deal of skill. The operator holds the bottle in a slanting position and gradually loosens the cork until it is thrown out by the pressure together with the whole sediment. At the same instant the bottle must be turned upright and preliminarily closed. Some sugar solution is added before the bottles are finally corked, the quantity varying greatly according to the requirements of the trade. The sugar solution is thoroughly distributed by shaking and the bottles preferably kept in stock for some time before being consumed in order that the taste be more harmonious and the carbonic acid more permanently bound.

Imitation champagne is made by saturating white wine with carbonic acid under pressure in a suitable apparatus, but such sparkling wines are generally lacking in life and, when poured into the glass, do not show the same permanent sparkling as those made by the slow process of bottle fermentation.

XXXVI

DISTILLED LIQUORS

ALLEN ROGERS

THIS industry differs from the two already described in that the effort is made to carry the fermentation to the limit, so as to obtain the maximum quantity of alcohol, the product being then distilled in order to secure a distillate richer in alcohol than the fermentation product. The end desired may either be an alcoholic beverage or a raw spirit. By further distillation "rectified spirits" may be obtained, which may be used in the production of alcoholic beverages, or as a solvent in many manufacturing operations.

Alcohol. In this country grain is usually employed for the manufacture of alcohol, while in some of the European countries potatoes are more largely used. The first stage in the process consists in the saccharifying of the starch of the grain. It is customary to mix a small amount of malted grain with raw grain, as by so doing a small quantity of diastase can be made to convert a large amount of starch into maltose or fermentable sugar. The ground mixture of raw and malted grain is placed in a mashtub and agitated with water at a temperature of 146° F. As the object of the distillation is to convert as much of the starch as possible into maltose, the temperature must not be allowed to rise above this point, otherwise the amount of maltose will decrease and the dextrine, which is not fermentable, will increase. As the wort reaches its full density it is drawn off and fresh water at 190° F. introduced. The second wort so obtained is added to the first. A third wort is sometimes made which is then used on fresh grain. The extract is now rapidly cooled to the temperature of fermentation, so that acetous fermentation will not set in. The temperature of fermentation is from 92 to 94° F., except when the entire mash is used, both solid and liquid portion, when the fermentation takes place at a much lower temperature. The time of fermentation varies from three to nine days. The "coefficient of purity" of a fermentation is a term employed to show the percentage of available starchy matter which has undergone alcoholic fermentation. Although grain and potatoes are used very largely for alcohol and spirit manufacture, other materials, especially beet and cane-sugar molasses, are quite widely employed.

Distillation. On reaching the limit of fermentation the product is distilled. This may be carried out in a crude manner by the old form of still with worm condenser. Modern fractionating apparatus, however, has superseded this method in the majority of places. The various forms of stills described in Chapter I, are all more or less in common use. The products from the preliminary distillation, however, are not sufficiently strong and must be strengthened by rectifying.

Rectifying. By redistilling the weak product, "doubling," obtained from the first distillate a crude milky spirit, rich in oil, first comes over, followed by a clear spirit, the latter being caught in a separate vessel. The last portion, being weak in strength, called "faints," is returned to the weak spirit and again subjected to distillation. Rectifying is usually conducted in column stills, by which a very pure alcohol may be obtained in one or two distillations.

Raw spirits even up to 90 per cent purity contain quite an amount of fusel oil (propyl, isobutyl, and amyl alcohols), which must be considered in the manufacture of alcoholic beverages. Some acetaldehyde also remains, which gives to the raw spirit a bitter taste. Various methods have been proposed to remove the foreign bodies, but the most recent is to treat the diluted spirit with petroleum oil, which has the power to absorb the fusel oil, thus withdrawing it from the dilute alcohol.

Rectified Spirit. This is a name given to the most concentrated alcohol which it is possible to produce by distillation.

Proof Spirits. This is a term used to quite an extent in England for excise purposes. Its strength, as defined by Parliament, is such that thirteen volumes shall weigh the same as twelve volumes of water at 51° F. Proof spirit so made will have a specific gravity of 0.9198 at 60° F. (15.5° C.) and contain 49.24 per cent of alcohol by weight. Spirits weaker than proof are described as U.P. (under proof), and stronger than proof as O.P. (over proof); thus 50 U.P. means 50 parts of proof spirits and 50 parts of water, while 50 O.P. means that for each 100 parts of spirit 50 parts of water must be added to reduce it to proof.

Arrack. This is a liquor distilled from the fermented juice of the cocoanut palm, *toddy*, or from malted rice. The arrack from Goa and Columbo is supposed to be the best and is made entirely from toddy. The juice of the cocoanut palm is obtained by making an incision in the tree and collecting in cups hung under the cut. It is then fermented and subsequently distilled.

Brandy. Pure *cognac* is obtained from the distillation of French white wine. Its flavor and aroma are due to the presence of ethyl pelargonate. The inferior varieties come from the distillation of the red Spanish and Portuguese wines or from the marc and refuse from the wine press. Much brandy is also made artificially from spirits and water to which coloring and flavoring materials have been added. When first distilled, brandy is colorless, and will remain so if kept in glass bottles, being known

as *white brandy.* It is customary, however, to store it in oak casks, from which it takes up a yellow tint, being known as *pale brandy.* A deeper color is often given to brandy by the addition of caramel.

Kirschwasser. This is a spiritous liquor obtained in the Black Forests and Switzerland by the distillation of fermented cherries. The sound fruit only is taken and the juice expressed. The stones are then crushed separately and added to the juice, the whole being fermented and subsequently distilled. It is a colorless liquor with an agreeable odor and flavor which improves on standing.

Rum. This liquor is obtained from the fermentation of cane-sugar molasses. It is made in the West Indies, Jamaica, Martinique, Guadeloupe, and formerly to quite an extent in New England. When new, it is colorless and has an unpleasant odor which is eliminated by treatment with lime and charcoal. The characteristic flavor of rum is due to the presence of butyric ether, which compound is also prepared artificially and is known as *rum essence.* Rum is always colored with caramel.

Whiskey. This spirit is obtained from either the raw or malted wort of corn, rye and barley. In the preparation of Kentucky whiskey partially malted rye and corn are used, while in some other localities only rye is employed. In Scotland and Ireland malted barley is the chief grain taken, the difference between the two whiskeys being that the former is distilled in Coffey stills and is thus deprived of its essential oils, while the latter is distilled in crude pot-stills which permits the oils to pass over with the distillate.

Gin. This is a common grain spirit distilled in the presence of juniper berries, which gives to the distillate the peculiar flavor of the berry. The finest gin is made in Schiedam, Holland, whence the name "Schiedam Schnapps."

Cordials. This name is given to the spirituous liquors obtained by steeping fruits or aromatic herbs in brandy or other spirits and subjecting the resulting liquid to distillation. They are then colored and usually sweetened.

Absinthe. The best known of the cordials is absinthe, which is obtained by distilling brandy in the presence of wormwood. The product therefore contains the oil of wormwood, which causes a deletereous effect upon the nervous system, it is claimed. The amount of oil in absinthe is so great that the liquid becomes turbid when diluted with water.

Among the other cordials should be mentioned: *Anisette, Chartreuse, Curacoa, Maraschino, Ratifia, Usequebaugh, Benedictine, Kummel,* and *Creme de menthe.*

XXXVII

TEXTILES

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Definitions. By the term "textiles" is to be understood a class of manufactured articles prepared from "yarns" which are continuous threads composed of fibrous materials. These fibrous materials which form the basis of textile manufactures are of various kinds, including animal, vegetable, and mineral products; for example, wool, cotton, and asbestos. A fiber is really a filament the length of which is comparatively much greater than the diameter, and the latter is of almost microscopic proportions. This allows of several fibers being twisted together by a process known as spinning, so that a continuous and uniform thread is produced. Physically, a textile fiber must possess considerable tensile strength and pliability in order to yield a satisfactory thread. In the case of the shorter fibers, such as cotton and wool, the surface structure also allows of considerable cohesion between the separate fibers when twisted together. Where this cohesive property is lacking, as in silk and some of the cruder vegetable fibers, the strength of the twisted thread depends on the great length of the individual filaments.

Origin. The textile fibers may be classified with respect to their origin in the following manner:

Animal Fibers, consisting (*a*) of the hairy covering of various animals, principally of the sheep, goat, cow, and camel; and (*b*) of the filaments spun by the silk-worm for its cocoon.

Vegetable Fibers, consisting (*a*) of the hairy covering of the seed of the cotton plant; (*b*) of the bast or structural part of the stem of certain plants such as flax, ramie, jute, and hemp; (*c*) of the structural part of the leaves of such plants as sisal, agave, and certain palms.

Mineral Fibers, of which the only representative is asbestos.

Artificial Fibers, such as artificial silk prepared from solutions of cellulose derivatives, spun glass, and certain metals drawn out to fine filaments.

The great bulk of the textile fibers are comprised under the first two classes, of which the most typical representatives to be considered are: wool, silk, cotton, and linen.

The Animal Fibers. In their chemical nature these fibers are essentially proteid substances of complex organic structure. The basis of wool (and the hair fibers in general) is called *keratin*, a nitrogenous substance containing also sulphur, while that of silk is known as *fibroin*, which is also nitrogenous but does not contain sulphur. In their physical structure the hair fibers are very complex, being composed of minute cells and provided with an external layer or sheath of hard, bone-like tissue or scales. Silk, on the other hand, is a continuous filament without apparent organic structure.

The Vegetable Fibers. The chemical basis of this entire class of fibers is *cellulose*, and as this contains neither nitrogen nor sulphur, it presents a marked chemical difference to the albuminous substance of the animal fibers. In their physical structure the vegetable fibers as a class are comparatively simple; in the case of cotton the fiber consists of a single elongated cell; with the bast and leaf tissues the commercial fiber consists of a more or less complex aggregate of small cells. Cotton in its natural state, consists of almost pure cellulose and requires but little purification for use in manufacturing; the other vegetable fibers, however, are associated with a considerable amount of substances other than cellulose and require a rather extensive process of purification for the purpose of isolating the pure cellulose fiber.

Wool. This fiber is the hairy covering (or fleece) of the sheep. It is a growth originating in the skin, springing from a root or hair-follicle. In its physical structure the fiber consists of three portions: (*a*) an inner layer of rounded elliptical cells, called the *medulla*, and often containing pigment matter; (*b*) a surrounding region of elongated spindle-shaped cells, called the *cortical* layer, which forms the major portion of the fiber; and (*c*) an external coating of flattened, hard horn-like cells, or *epidermal scales*, arranged in such a manner as to overlap like the scales on a fish. This latter peculiarity of structure gives to wool a characteristic microscopic appearance whereby it may be readily distinguished from other fibers (see Fig. 321). The character of fiber produced in the fleece varies largely with the breed and cultivation of the sheep. The merino sheep (now grown principally in Australia) gives a long, fine and wavy fiber, much prized for the manufacture of high-class clothing fabrics. The majority of the wool grown in America (chiefly known by the name of "territory" wool) is of shorter staple and coarser in quality. The arrangement of the epidermal scales also varies considerably with the nature of the fiber. With some wools, these scales are prominent and the free edge projects considerably, giving the fiber a serrated or saw-toothed appearance. Wool of this nature is easily *felted*

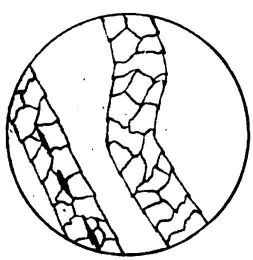

FIG. 321.—Typical Wool Fiber.

as the fibers become firmly attached to one another by the interlocking of the projecting scales. In other varieties of wool the external scales lie flat on the surface with very little free edge projecting, hence the surface of these fibers are smooth and do not readily felt together. Another important physical property of wool is its waviness. Some wools (especially the fine merinos) are very wavy, and the waves (or crimps) occur with great regularity throughout the entire length of the fiber; other wools are stiff and straight with little or no waviness, or have very irregular waves. The wavy structure of the fiber enhances its spinning quality, as it allows of a greater coherence among the fibers when they are twisted together. A yarn composed of such fibers also exhibits greater resiliency and sponginess as well as elasticity.

In its *chemical properties* wool is closely allied to gelatin and horn-tissue. It probably consists of a number of chemical bodies, as its proximate chemical composition varies considerably in different samples. Its average composition may be taken as follows:

	Per Cent.
Carbon	50
Hydrogen	7
Oxygen	26–22
Nitrogen	15–17
Sulphur	2–4

From its general chemical reactions the substance of the wool fiber has been classified as a proteid to which the name *keratin* has been given. This probably contains both amino and acid radicles in its constitution, as it exhibits in a well defined manner both basic and acid properties. The amino-acid existing in wool has received the name *lanuginic acid*, and it may be prepared by dissolving the fiber in barium hydroxide solution, treating with carbon dioxide to precipitate the barium, filtering, and adding lead acetate which precipitates the lead salt of lanuginic acid. The free acid itself may be obtained by decomposing the lead salt with hydrogen sulphide. Lanuginic acid is soluble in water and yields the same reactions with mordants and dyestuffs as wool itself. The wool fiber is rather sensitive to the action of high temperatures; if exposed to a dry heat of over 100° C. the fiber soon becomes discolored, harsh and brittle. On this account the drying of woolen materials should be carefully conducted to avoid injury. Strong solutions of mineral acids destroy the wool fiber, though dilute solutions are without injury. Sulphuric acid in dilute solution apparently combines in a chemical manner with wool, causing the fiber to become more reactive towards many dyestuffs. Nitric acid gives wool a yellow coloration, supposedly due to the formation of xanthoproteic acid. Nitrous acid apparently causes a diazotization of the amino radicle in wool, for when so treated the fiber combines with various phenols, with the production of a number of colors. Solutions

of alkalies (especially the caustic alkalies) react injurious, with the wool fiber; with even dilute solutions of sodium hydrate wool is rapidly dissolved. This reaction permits of the easy chemical separation of wool from cotton for analytical purposes. With solutions of metallic salts (such as potassium dichromate, alum, ferrous sulphate, etc.) wool reacts in apparently a chemical manner, as it combines with the metallic oxide, and in this condition is capable of uniting with many dyestuffs. This process is termed *mordanting* and the metallic salts employed are known as mordants. When wool is treated with solutions of bleaching powder a product known as *chlorinated* wool is produced; the fiber becomes glossy, harsh, and loses its felting properties.

Scouring of Wool. In its natural state in the fleece wool is contaminated with a number of impurities. These may be classified as follows:

(*a*) *Wool grease,* which occurs in large quantities as an external coating on the fiber; it is a natural exudation of the sheep and serves as a protection to the fiber, preventing it from becoming felted and mechanically injured. It differs from other animal fats in that it does not consist of the glycerides of the fatty acids, and is very difficultly saponifiable with caustic alkalies. Wool grease possesses more the chemical properties of a wax, as it is composed mostly of the higher solid alcohols known as cholesterin and isocholesterin both in the free state and as esters with the fatty acids. Though insoluble in water and not saponifiable by alkalis, cholesterin is easily emulsified, a property on which is based the usual method of wool scouring. Wool grease, however, is easily soluble in naphtha and other volatile solvents.

(*b*) *Suint,* or dried-up perspiration, consisting largely of potash salts of organic acids, and soluble in water.

(*c*) *Miscellaneous dirt,* such as dust, sand, vegetable matters, tar, etc.

Before the wool fiber can be used in manufacturing processes it must first be cleansed from the adhering impurities. This is accomplished by scouring the dirty and greasy wool in a warm soap solution, to which more or less soda ash is added. The temperature of scouring should not be above 140° F., else the fiber will be injured by the action of the alkali. The wool grease is easily emulsified by the alkaline soap solution, whereas the suint is dissolved by the water, the other impurities being removed by the mechanical action of the water. After scouring in the soap solution the wool is thoroughly rinsed in warm water, and finally squeezed and dried. Another form of wool scouring, known as the *solvent process,* is becoming of great importance in this country. The greasy wool is treated with solvent naphtha in closed kiers, and the resulting solution of wool grease is transferred to stills where the naphtha is recovered and the wool grease is obtained as a by-product. The latter may be further purified and utilized for the preparation of *lanolin* compounds. The degreased wool is next treated with a dilute warm soap solution to remove

the suint and dirt. This process leaves the fiber in a much better condition and the recovered grease is of sufficient value to pay for the cost of scouring.

The potash salts existing in wool suint and removed by the scouring are valuable by-products which are capable of recovery. In many European plants these salts, as well as the grease, are recovered and utilized; in this country, however, the wash waters containing the suint are run to waste. The amount of grease and dirt in wool varies greatly with the breed and cultivation of the sheep. The finer stapled wools usually contain the largest proportion of grease. The amount of dirt and vegetable matter will depend largely on the character of the range on which the sheep are grown; a dry sandy soil usually producing a large amount of dust in the wool. The amount of loss caused in scouring wool is known as its *shrinkage* and this amounts to 40 to 70 per cent on the weight of the raw fleece. In America, as a rule, there is no distinction made between the wool grease and the suint but the total impurities in the fleece are known under the name of *yolk*, as in the usual emulsion process of scouring the entire impurities are removed *in toto* in a single operation.

The scouring of wool is usually conducted by machinery with the object of agitating the fiber in the least possible degree so as to avoid felting. The machines in general use are long tanks arranged in tandem order. The greasy wool is introduced into the first tank by means of a traveling apron, and is slowly carried through the scouring liquor by moving forks until it is caught up by squeeze rolls and passed into the second tank, where it is carried forward in the same manner through another soap solution; it is finally carried through a third tank containing fresh warm water for rinsing. The scouring liquor is introduced fresh into the second tank and passes thence into the first tank, so as to have the clean wool coming from the fresh liquor. In some places the spent scouring liquors are worked up to recover the potash salts by simple evaporation and calcination, when from 5 to 10 per cent (on the weight of the raw wool) potash may be obtained. Again, the spent liquors are sometimes treated with sulphuric acid in order to decompose the soaps and liberate the fatty matters. The latter, together with the associated wool grease, are settled out on the surface of the liquor from which they are removed. The excess of water is eliminated by hot pressing in bags. The crude greasy product so obtained is known as *Yorkshire grease*, and has considerable use for dressing leather and as a lubricating grease.

Mechanical Treatment of Wool in Manufacture. After wool has been scoured and dried the next step is to convert it into yarn. In the first place, according to the quality of yarn desired, a close selection of the required grade of wool is made. This is the function of a special branch of the industry known as *wool grading and sorting*. Wool is first graded with reference to the breed of sheep, such as full-blood merino, territory, half blood, etc. This has reference chiefly to the fineness and

length of staple. The long stapled wools are suitable for *combing* and are used for the preparation of *worsted* yarns; the shorter stapled varieties are *carded* and made into *woolen* yarns. In the combing process the shorter fibers (*noils*) are removed from the long ones, leaving the latter to form what is called *tops*, a form of preparation previous to the spinning of the yarn. As the character and equality of the fiber varies considerably at different parts of the same fleece, wool is further graded by *sorting* the fleece into its distinctive portions, such as the loin, back, neck, legs, etc. Usually the fleece is sorted into nine portions. The grading and sorting of the fleece is made previous to scouring.

In the preparation of yarn the first step is combing (for long staples) or carding (short staples). This is for the purpose of removing undesirable matters, such as short fibers, adhering impurities, etc., and also to lay the fibers in a parallel direction and bring the wool into a ribbon-like form so as to permit of the subsequent spinning operations. These latter processes consist in further paralleling the fibers and reducing the thread to the desired size by drawing out and twisting.

Chemical Treatment of Wool in Manufacture. (1) *Bleaching.* The wool fiber in its natural state contains more or less of a yellowish brown pigment. In some cases this pigment becomes greatly accentuated and the fleece may be dark brown or even black in color, but these occasional "black sheep" are of rather rare occurrence. Where it is desirable to have a perfectly white fiber either for purposes of dyeing delicate tints or for white goods, it becomes necessary to bleach the wool. There are two general methods in use at present for this purpose. In the first, sulphurous acid, SO_2, is used as the active bleaching agent. The well scoured and moistened woolen material is placed in a suitable room and subjected to the prolonged action of fumes of burning sulphur, the time required for complete bleaching being from eight to twenty-four hours, depending on the nature and texture of the material. The process is termed "stoving," from the so-called stove in which the sulphur is burnt. The bleaching room must be so constructed as not to permit of the condensed acid liquor dropping on the goods, which would otherwise be spotted and injured. This process is known as the "gas" or "dry" method of bleaching. After the bleaching is finished the wool is rinsed in a water containing a minute quantity of a blue or bluish-violet coloring matter for the purpose of tinting the white so as to furnish a more pleasing color to the eye. A "wet" process of bleaching may also be employed, the wool being steeped in a dilute solution of sodium bisulphite for some hours, and then passed through a bath of dilute sulphuric acid. The bleached white obtained on wool with sulphurous acid does not appear to be permanent, as prolonged exposure to the air will cause the yellow natural color to return. This has been accounted for by assuming that the sulphurous acid merely reduces the natural pigment to a colorless compound

which becomes reoxidized on exposure to the air, resulting in the formation again of the original pigment.

A second process for the bleaching of wool which is coming into considerable favor more especially for fine goods is that which employs sodium peroxide as the bleaching agent. Formerly hydrogen peroxide was used somewhat in bleaching, but its cost is too high for general purposes. Sodium peroxide, Na_2O_2, when dissolved in water acidulated with sulphuric acid, yields a solution of sodium sulphate and hydrogen peroxide:

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

The hydrogen peroxide in contact with organic substances readily decomposes with liberation of nascent oxygen:

$$H_2O_2 = H_2O + O,$$

and the latter quickly decomposes and destroys the coloring matters in wool. In general outline, then, the process of bleaching wool with sodium peroxide is to prepare a bleaching liquor as follows:

100 gals. of pure water;
5 lbs. 5 ozs. oil of vitriol (168° F.);
4 lbs. of sodium peroxide (98 per cent).

The acid is mixed with the water first and then the sodium peroxide is carefully sifted in. These proportions should leave the bath in a slightly acid condition; this is essential, as otherwise caustic soda would be present from the incomplete neutralization of the sodium peroxide, and small traces of that alkali in the bath would be very injurious to the fiber. Before using the bath for bleaching it is neutralized by the addition of the requisite amount of sodium silicate, ammonia, or borax. This is necessary because the bleaching effect is much enhanced in a slightly alkaline solution. The woolen material (which has previously been well scoured) is then entered and manipulated sufficiently to thoroughly saturate the fibers, after which the wool is left in the liquor for ten to twenty hours when the bleaching should be complete. All the materials employed in the preparation of the sodium peroxide bath must be very free from iron, otherwise the bleaching will be imperfect. The bleaching vat should be of wood and all necessary pipes should be of lead. The temperature of the bath should be maintained at about 100° F. during the entire time of bleaching. The white color obtained by this method of bleaching is a permanent one as the pigment matter in the fiber is completely destroyed. It also leaves the fiber free from any deleterious substance, hence is to be preferred to the sulphur method which nearly always leaves a residue of sulphurous acid (or its compounds), and this

acts injuriously on many coloring matters which may be used in the after-dyeing of the bleached wool. Unfortunately the cost of the sodium peroxide method is still too high to permit of its general adoption.

Wool may also be bleached by treatment with a cold dilute solution of potassium permanganate. The pigment in the fiber is rapidly destroyed by the strong oxidizing action of this chemical, but the resulting decomposition of the permanganate precipitates a brown hydroxide of manganese on the fiber, hence it is necessary to pass the wool through a second bath containing a weak solution of sodium bisulphite which removes completely the deposit of manganese compound and leaves the wool perfectly white. This method gives a very rapid process for bleaching, but it is rather costly. Wool, however, which had been bleached with sulphurous acid, is often treated with a very dilute solution of potassium permanganate to insure the complete removal of all residual sulphurous acid compounds from the fiber. Wool may be bleached in almost any stage of its manufacture; as loose stock, tops, yarn, or cloth.

Carbonizing. Woolen material is often contaminated with small quantities of vegetable fiber, and as the latter does not become dyed in the same manner as the wool, it shows itself in the form of specks. To purify the cloth (or other form of manufactured wool) from these specks, the vegetable fiber is destroyed by treatment with a dilute solution of sulphuric acid (6° Tw.) and subsequently drying at 180 to 190° F. This "carbonizes" the vegetable matter, or reduces it to a brittle friable substance, which is easily removed by beating and washing the woolen material. Dilute solutions of aluminium chloride (10 to 12° Tw.) may also be used for the same purpose, as on drying this salt is decomposed with liberation of hydrochloric acid. The latter method is used chiefly where dyed materials are to be treated, as the colors are less affected than when sulphuric acid is employed. The process of carbonizing is also largely employed for the purpose of recovering the pure wool fiber from rags containing mixtures of wool and cotton yarns. The resulting product is known as *shoddy* or *mungo* and has a large use in the woolen industry.

Crabbing. This is a process for removing the crinkle or curl from cloth or yarn caused by the uneven shrinkage or curl of the fiber. It depends on the fact that when the wool fiber is subjected to a moist heat it becomes plastic and can easily be straightened out by stretching. If the fiber is then cooled in the stretched condition it will preserve its straight form permanently. Tightly twisted worsted yarns are very liable to curl up. This may be remedied by treating the stretched yarn with steam or boiling water, and then allowing to cool while still in the stretched condition. Cloth containing tightly twisted or curled yarns or containing a mixture of woolen and cotton yarns will crinkle up or pucker owing to uneven contraction of the yarns in finishing. This may be removed by passing the stretched cloth alternately through boiling water and cold water, or better yet by tightly winding the cloth on a perforated cylinder

and blowing steam through it, then subsequently cooling. The crabbing process in the case of cloth is also known as *decatizing*.

Fulling. This process is also known as "milling." It is a felting action produced on the wool fibers in a fabric by the combined action of soap and friction. The projecting scales on the individual fibers become interlocked so that the fibers firmly adhere together. This action causes the cloth to shrink considerably and at the same time become more continuous and homogeneous in its structure. If the operation of fulling is carried on to its full extent a *felt* is made of the cloth. Acid solutions, and even boiling water, combined with friction will also produce fulling. In this manner hat felts are produced.

The Minor Animal Fibers. In addition to wool there are also a number of other animal hair fibers employed to a limited extent in the manufacture of textiles. The woolly fibers of different species of goats are utilized in much the same manner as wool itself. *Mohair* is obtained from the Angora goat. The fiber is long, fine, smooth and highly lustrous. It is largely used for the manufacture of plushes, braids, and linings. *Cashmere*, *alpaca*, and *llama* are also fibers from species of goats. All of these animal hair fibers are similar in chemical composition to wool; their physical structure is also very similar.

Silk. Though silk is also an animal fiber and somewhat similar to wool in its general chemical properties, it differs very widely from that fiber in its physical structure and properties. The silk fiber is a fine continuous filament spun by the silkworm in the preparation of its cocoon. The fiber as spun by the caterpillar consists of two filaments composed of a proteoid substance called *fibroin* and surrounded and cemented together by a glue-like substance known as *sericin* or silk-gum. The silkworms are cultivated principally in China, Japan, Italy, and southern France. Their chief food consists of the leaves of the mulberry tree, hence the caterpillar is known as the mulberry silkworm, or *Bombyx mori*. The cocoons are irregularly ovoid in shape and the length of the fiber in them varies from 350 to 1200 meters, while its average diameter is 0.018 mm. The silk fiber as used in manufacturing is prepared by *reeling* from the cocoons. When the cocoons have been completed by the silkworm they are collected and heated in an oven to a temperature of 60 to 70° C. for the purpose of killing the pupa within. Or, the cocoons may be steamed for a few minutes which serves the same purpose. The cocoons are then sorted for size, color, damage, etc., so as to obtain a uniform product. They are then placed in a basin of warm water which softens the enveloping silk-glue and permits of the unwinding of the cocoon thread. The fibers from several cocoons are brought together and passed over a suitable reel where they are slightly twisted together to form a thread of sufficient size for weaving. The adhering silk-glue becomes hardened again, so that the thread presents a uniform appearance. This silk is reeled into skeins of convenient size and comes into

trade as *raw silk.* Owing to the presence of the silk-glue it is stiff and wiry and translucent in appearance. Some varieties are of a creamy white color, while others are quite yellow. This yellow color, however, exists only in the silk-glue and is removed along with the latter. *Organzine* silk is prepared from the highest grade of cocoons, and by reason of its superior strength it is employed for warps. *Tram* silk is weaker and is used for filling. In the reeling of silk a large amount of waste is produced. This is scoured in a solution of soap and soda in order to remove the silk-glue, and the residual fiber is then carded and combed and is used for the preparation of *spun silk.*

Boiling-off of Silk. The reeled silk as it appears in trade consists of 70 to 75 per cent of fibroin or fiber proper and 30 to 25 per cent of sericin or silk-glue. For purposes of manufacture it is necessary to remove more or less of the silk-glue. For this purpose the skeins of raw silk are treated near the boil in a strong solution of soap (about 1 lb. per gallon). The soap must be of the best quality and free from uncombined alkali as the quality of the silk is greatly deteriorated by the presence of even a trace of the latter substance. When all of the silk-glue is to be removed it will be necessary to boil the silk for several hours in two or more soap solutions. It is best to maintain the temperature just under the boiling-point to prevent the tangling of the fine silk fibers. The soap solutions are used continuously for the boiling-out of several batches of silk until they became heavily charged with dissolved silk-glue. The spent soap solution is known as *boiled-off liquor* and is largely used in the preparation of the dye-bath for silk. Boiled-off silk will shrink about 25 per cent in weight. More frequently it is not desirable to remove all of the silk glne, but only sufficient to allow of the fiber being subsequently dyed, bleached, or otherwise processed. When 10 to 15 per cent in weight is lost by scouring the process is termed *soupling.* When the boiling-off removes only 2 to 5 per cent in weight the product is known as *écru* silk.

The Chemical Nature and Properties of Silk. Though silk is somewhat similar to wool in its general chemical properties it differs from that fiber in that it does not contain any sulphur in its composition. Silk is readily attacked by alkalies, especially in hot solutions, though it is more resistant in this respect than wool. The caustic alkalies slowly dissolve the silk fiber on boiling, whereas the alkaline carbonates are much less destructive, but even these reagents slowly attack the fiber. Concentrated hydrochloric acid rapidly dissolves silk even when cold. Dilute mineral acids are absorbed by the fiber in the same manner as with wool, and may be employed in the dyeing of silk. Dilute solutions of nitric acid are employed for the bleaching of silk. The effect of dilute acid solutions on silk, especially when dried into the fiber, is to increase somewhat the luster and to give the silk what is called *scroop*—that is, it produces a crackling rustling sound when rubbed or compressed. This property is best imparted by steeping the silk in a bath of dilute acetic,

tartaric, or formic acid, squeezing and drying without washing. Hard water (containing lime) should be avoided when dyeing or bleaching silk, as it affects the luster of the fiber, and makes it brittle. Chlorine, and oxidizing agents in general, rapidly destroy the silk fiber, except when employed in very dilute solutions. Silk is capable of absorbing metallic salts from solutions and fixing the oxide of the metal in the fiber. On this action is based the process of mordanting and weighting silk. Tannic acid is also absorbed by the fiber in large proportions. For purposes of mordanting, silk is steeped successively in baths containing tannic acid (cutch, myrabolams, etc.) and an iron salt (such as pyrolignite of iron or "nitrate of iron," which is really a ferric sulphate). By repeating these treatments a number of times the silk may be *weighted* to a considerable extent, frequently as much as 100 per cent. This method of weighting is principally used as a preparation for the black dyeing of silk. Where colors are to be dyed, the silk is usually weighted with tin phosphate, the fiber being treated with baths of stannic chloride, sodium phosphate, and sodium silicate. A high degree of weighting can also be obtained in this manner.

The proximate composition of the fibroin of silk is as follows:

Carbon	48.3%
Hydrogen	6.5
Oxygen	26.0
Nitrogen	19.2
	100.0

These figures refer to the purified fibroin free from all silk-glue or other contaminating substances. As different samples of silk give slightly different results on analysis, it is probable that the silk fiber is a composite substance and not an individual chemical body. The sericin, or silk-glue, has the following composition:

Carbon	48.8%
Hydrogen	6.2
Oxygen	26.0
Nitrogen	19.0
	100.0

Thus it will be seen that the sericin is very close to the fibroin in its chemical composition. The former, however, is slowly soluble in warm water and readily soluble in soap and alkaline solutions, whereas the fibroin is not.

Physical Properties of Silk. When examined under the microscope the raw silk fiber is found to consist of two more or less parallel filaments more or less firmly cemented together by an envelope of silk-glue. Due

to the process of reeling from the cocoon, irregular shreds and lumps of silk-glue will also be noticed adhering to the fibers (see Fig. 322). This microscopic appearance of silk is quite characteristic, and serves to distinguish it from other fibers. No indication of internal structure can be noticed in the case of the purified fiber; it merely resembles a translucent glass rod, smooth and regularly cylindrical.

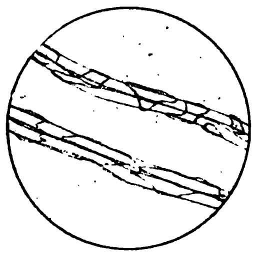

FIG. 322.—Silk Fiber. Cocoon threads showing double filaments and adhering silk glue.

As already noted raw silk is harsh and wiry in handle and rather lusterless in appearance. This is due to the envelope of silk-glue surrounding the fiber. When this is removed the fiber proper appears as a white, soft, and highly lustrous fiber. It possesses a remarkably high tensile strength and great elasticity. Silk is also a good non-conductor of heat and electricity.

Wild Silks. Besides the ordinary variety of cultivated or mulberry silkworm, there are a number of other silkworms which grow wild, yet furnish cocoons which yield a considerable amount of commercial silk. This fiber is generally known under the name of *tussah* or *tussur* silk. It is of a brownish color, and is harsher and coarser than mulberry silk. It is also much harder to boil off and to bleach and dye. It is largely used for the manufacture of plush fabrics, imitation sealskin, etc., and also for a dress material known as " pongee " or tussur silk. Wild silk can readily be distinguished under the microscope, as the fibers are broad, and the cross-section is flat and triangular. Longitudinal striations are also very distinct, as well as peculiar oblique cross-markings caused by the overlapping of the fibers on one another in the cocoon before the fibroin has become hardened.

Bleaching of Silk. For most purposes silk is sufficiently white without bleaching, but where very delicate tints are to be dyed or where a very pure white fabric is desired, it is necessary to bleach out the slight tint of yellow to be noticed in natural silk. Silk may be bleached in much the same manner as wool, using either the sulphurous acid or the sodium peroxide process. The latter method is to be preferred in the case of silk, as it furnishes a nicer product, and the bleach is not liable to become yellow again on exposure. The extra cost of this process is not a drawback when employed for silk as when used for wool, as the comparative value of the fiber itself is far greater. Silk is also bleached by treatment with dilute cold solutions of *aqua regia*. This method is generally employed in the case of soupled silk.

Cotton. The cotton fiber consists of the hairy covering of the seeds of the cotton plant, or *gossypium*. There are a large number of species and varieties of the cotton plant, the principal of which are the following:

Gossypium barbadense, producing silky and long-stapled fibers, the

principal representatives of which are the *Sea-Island* cotton of the Southern Gulf States, Egyptian cotton, and Peruvian.

Gossypium hirsutum, which includes most of the cotton grown in the United States and forms the great bulk of the cotton used in trade. It is known as *upland, peeler,* or simply *American* cotton.

Gossypium herbaceum, including the majority of the cotton grown in India and China, as well as the small amount which is grown in Italy. The fiber is very short and inferior to that of the two preceding varieties.

Gossypium arboreum, comprises most of the cotton in Asia Minor. This variety grows to the dimensions of a tree in contradistinction to the other varieties which are all shrubs. The fiber is of poor quality, being short and coarse and of a greenish color.

The seed hairs of cotton are developed in a boll as the fruit of the plant ripens, and when maturity is reached the boll bursts open liberating a fluffy white mass of fibers. These fibers are firmly attached to the surface of the seed, and after the cotton is picked from the plant the fiber must be detached and separated from the seed by a process known as *ginning.* The ginned fiber is then baled and distributed to the spinning mills. The seed which is left now forms a valuable by-product of the industry. It is first subjected to a second process of ginning for the purpose of removing the short undergrowth of fibers known as neps or linters, and these are used in the manufacture of wadding and cotton batting. The cleaned seeds are then hulled, and from the separated meal the oil is extracted by cold and hot pressing and steaming. The cottonseed oil so obtained is a very valuable product, the finer qualities being used for salad oils and other culinary purposes, while the lower grades are extensively used for soap-making. The residual meal is used as a cattle-food, and other residues find use as fertilizers.

Before being utilized by the spinner, cotton is graded with respect to length and fineness of staple, color, cleanliness, and other qualities. The value of the fiber is determined by this classification, the basis being what is known as " middling " cotton, the various grades going up and down from this standard.

Physical Properties of Cotton. The cotton fiber consists of a single cell, narrow and elongated, with one end fastened to the seed and the other tapering to a point. During its growth it is tubular, being cylindrical in shape with comparatively thin cell-walls and an inner canal or *lumen.* When the fiber ripens, the sap in the inner canal is absorbed, the cell-walls collapse, leaving a flat ribbon-like fiber with thickened edges. By the unequal drying of the fiber it becomes twisted spirally on its axis. These spiral twists give to cotton its good spinning qualities, for when twisted together the fibers cohere to one another to give a strong thread. The different varieties of cotton exhibit considerable variation in length and fineness of staple. Sea Island cotton has an average length of about 1.6 ins. and a diameter of 0.00065 in. Ordinary American

cotton varies from 1.5 to 0.75 in. in length and has a diameter of about 0.00075 in. Egyptian cotton has a staple slightly shorter than Sea Island, and of about the same fineness. The South American and Indian cottons are comparatively short and coarse, averaging about 1 in. in length and 0.00085 in. in diameter. The physical character of the fiber in any lot of cotton is very variable, hence in manufacturing it is necessary to separate the short fibers from the long by a process of combing or carding; the longer fibers being used for the better grade of yarns and the shorter fibers for the coarser yarns. The degree of ripeness of the fiber also determines its general character; unripe fibers have a very attenuated cell-wall and consequently are weak and brittle. The mature fiber has a thicker wall and a much greater strength. Sea-Island, American, and Indian cottons contain very little natural pigment, being quite white in appearance; the chief varieties of Egyptian cottons, however, are rather highly tinged with a brownish color which is quite distinctive. The microscopic appearance of cotton is quite characteristic and serves to distinguish it readily from other fibers either of animal or vegetable origin (see Fig. 323). The flat, twisted, ribbon-like appearance is very noticeable.

FIG. 323.—The Cotton Fiber.

Chemical Properties of Cotton. In common with all other vegetable fibers, cotton is composed essentially of *cellulose;* in fact, the purified fiber may be considered as almost chemically pure cellulose. In its natural condition, however, there is associated with the cellulose a small amount of waxy and oily matter, which evidently acts as a protective layer on the surface of the fiber. The composition of the natural fiber is about as follows:

Cellulose ($C_6H_{10}O_5$)	91.00
Waxy and fatty matters	0.50–0.40
Nitrogenous matter	0.70–0.50
Moisture	7.50–8.00
Ash (mineral matter)	0.10–0.12

The presence of the waxy coating on the raw fiber causes it to be water-repellent, hence difficult to impregnate with solutions. On this account, cotton material must be boiled out for dyeing or bleaching; that is to say, the wax must be removed by boiling in a dilute solution of caustic soda, soda ash, soap, or other alkaline substance. Certain oils, such as Turkey-red oil (sulphonated castor oil) also have the property of rapidly removing the cotton-wax. The presence of this wax, however, aids considerably in the spinning of cotton as it makes the fiber more plastic and coherent. On this account dyed and bleached cotton does not spin as satisfactorily

as raw cotton. In its general chemical reactions cotton behaves in the same manner as ordinary cellulose. The fiber becomes rapidly disintegrated by the action of mineral acids, even in comparatively dilute solutions, and this is especially true when any of the acid liquor is allowed to dry into the fiber. Hence, in all operations of dyeing, bleaching, etc., where cotton may come into contact with acid solutions, it is very necessary to thoroughly remove the acid by continued washing or to neutralize it by a treatment with an alkaline solution. The organic acids which are volatile (such as acetic and formic) do not have much effect on cotton, and in consequence are generally employed in operations where the use of an acid is required for this fiber. The non-volatile organic acids (such as tartaric and oxalic) when allowed to dry and crystallize in the fiber affect it injuriously. Concentrated sulphuric acid converts cotton into a product known as amyloid or vegetable parchment. Concentrated nitric acid reacts with cotton to form a series of nitrated celluloses known as *pyroxylins*, which are utilized for a variety of commercial purposes. Among these derivatives may be mentioned *guncotton*, which forms the basis of numerous high explosives; *collodion*, which is a solution of pyroxylin in a mixture of ether and alcohol, and which is extensively used in surgery and photography as well as for the production of artificial silk filaments; *celluloid*, obtained by dissolving nitrated cellulose in molten camphor. The decomposition product of cottonwith dilute mineral acid s is known as *hydrocellulose* or *oxycellulose;* the acid evidently produces a hydration of the cellulose molecule with a consequent breaking down of its organic structure. Tannic acid reacts in a special manner with cotton; solutions of this acid do not produce a weakening effect on the fiber, though the acid is absorbed by the cellulose apparently with some degree of chemical combination. This reaction is the basis of mordanting cotton for the dyeing of basic colors. Tungstic acid exhibits a similar reactivity toward cotton.

Dilute solutions of alkalies, under ordinary conditions, have no harmful effect on cotton even at a boiling temperature, consequently such solutions are universally employed for the cleansing or scouring of cotton and cotton goods in general. A concentrated solution (40 to 60° F.) of caustic soda has a remarkable effect on cotton. The cellulose apparently combines with the alkali, the fiber swells up, losing its flat ribbon-like appearance to become tubular and semi-transparent. This process is the basis of the modern method of *mercerizing*. The product of combination between cotton and caustic soda is known as *alkali-cellulose*; it is easily decomposed by treatment with water, giving a product known as *hydrated cellulose*, which is the final form of mercerized cotton. Alkali-cellulose is soluble in carbon disulphide, forming a thick viscous solution of cellulose xanthate known as *viscose*. This latter substance has various industrial applications, such as the preparation of artificial silk, paper sizing, transparent films, etc. Cotton is unlike wool in its reactivity

toward solutions of metallic salts; whereas the latter readily absorbs and combines with various metallic salts, cotton is especially inert in this respect. On this account cotton cannot be mordanted in the same manner as wool. With oxidizing agents such as chlorine, potassium permanganate, and chromic acid, cotton is readily converted into *oxycellulose*, a brittle friable substance. On this account care must be exercised in the bleaching of cotton with chloride of lime to prevent the too vigorous action of chlorine on the fiber. Cotton can withstand a much higher temperature than wool without decomposition, though when subjected to a heat of over 160° C. the fiber suffers structural decomposition.

Bleaching of Cotton. On account of the nature and the small amount of impurities present in the raw fiber, cotton does not require a previous scouring operation to fit it for manufacturing processes. Previous to dyeing, however, cotton must be scoured or " wet-out " for the purpose of removing the waxy coating so that the fiber may be able to easily absorb the dye solutions. This is accomplished by boiling the material in a weak solution of caustic soda, soda ash, soap, or Turkey-red oil. When cotton is to be bleached, not only the waxy coating must be removed to permit of wetting-out, but as far as possible all of the impurities on the fiber must be removed. This process is termed " boiling out." Cotton may be bleached in any form of its manufacture. It is occasionally bleached in the loose state before spinning, in which case special machines are employed which allow of the bleaching liquors being circulated through the cotton without motion of the fibers, so as to avoid matting and injury to the latter. Instead of boiling out with alkalies, cold water is circulated through the cotton under pressure, which has the effect of removing the majority of impurities on the fiber without materially dissolving the cotton-wax. Cold bleaching liquors, wash waters, acid solutions, etc., are then circulated in the same manner. The result is a bleached cotton which still retains considerable wax, so the spinning qualities of the fiber are not materially injured. If loose cotton is thoroughly boiled out and bleached in the usual manner, the fiber will be harsh and will not spin well. Cotton waste and linters are also bleached largely in the loose state for the preparation of absorbent cotton. In this case, as it is not necessary to retain the spinning qualities but to make the fiber as pure and as absorbent as possible, a very thorough boiling out with caustic soda is given before the bleaching.

Cotton yarn is very extensively bleached, both for white goods and as a preparation for the dyeing of delicate shades. The yarn in the form of skeins is usually bundled together and systematically packed into a closed iron kier. The latter is so constructed as to permit of the circulation of a boiling alkaline solution under pressure (5 to 10 lbs.) through the yarn. The boiling-out solution usually consists of a mixture of caustic soda and soda ash. Sometimes so-called " bleaching assistants " are used; these mostly consist of soda ash mixed with a small amount

of caustic soda and sodium silicate. For the proper boiling out of the yarn it is essential that the liquor be circulated evenly and thoroughly through the goods. The amount of alkali employed is about 2 to 3 per cent on the weight of the yarn, and the time of boiling varies from one and one-half to eight hours, depending on the kier employed and the pressure. Overboiling by the use of too much alkali or too prolonged a treatment will render the yarn harsh and brittle and also cause yellow stains. The presence of air in contact with the superheated yarn in the kier will also cause oxidation resulting in weak places and stains. After the yarn has been boiled out it is washed with fresh water, usually in the same kier, and then worked in a cold dilute solution of chloride of lime (bleaching powder or chemic) at $1\frac{1}{2}$ to 2° Tw. For this purpose the yarn is either hung in sticks and steeped in the chemic solution in ordinary dye-house vats, or better yet it is placed in a machine (such as a Klauder-Weldon skein machine) where it may be automatically worked in the solution. The treatment with the bleaching liquor usually lasts from three-quarters to one hour. The yarn is then rinsed in fresh water and next *soured* by treatment with a cold solution of sulphuric acid at about 1° Tw.; hydrochloric acid may also be used. The acid treatment is for the purpose of decomposing the lime compounds retained by the fiber. Where sulphuric acid is used calcium sulphate is formed, which is easily removed in the subsequent washing. Hypochlorous acid and free chlorine are also liberated in the fiber which furthers the first bleaching action of the chloride of lime solution. This is evidenced by the fact that the cotton becomes much whiter in appearance when treated with the acid; also the presence of chlorine is to be noted from its pungent odor. When hydrochloric acid is used for the souring, the very soluble calcium chloride is formed which is very easily removed from the cotton by washing; otherwise the action of the acid is the same. After the acid treatment, it is necessary

FIG. 324.—Circulating kier for boiling-out of cotton. Jefferson type

FIG. 325.—Machine for bleach cotton skein yarns (Klauder-Weldon).

toward solutions of metallic salts; whereas the latter readily absorbs and combines with various metallic salts, cotton is especially inert in this respect. On this account cotton cannot be mordanted in the same manner as wool. With oxidizing agents such as chlorine, potassium permanganate, and chromic acid, cotton is readily converted into *oxycellulose*, a brittle friable substance. On this account care must be exercised in the bleaching of cotton with chloride of lime to prevent the too vigorous action of chlorine on the fiber. Cotton can withstand a much higher temperature than wool without decomposition, though when subjected to a heat of over 160° C. the fiber suffers structural decomposition.

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to give the cotton a very thorough washing to remove as completely as possible the residual acid liquor and the lime compounds from the fiber. If this is not done the yarn will be harsh and tender after drying. The washing should be continued until the yarn shows no indication of acid when tested with blue litmus paper. Finally, the yarn is treated in a dilute lukewarm solution of soap or other suitable finishing compound, and if a bluish tone of white is desirable a suitable bluish violet coloring matter is added for tinting purposes. The bleaching process with chloride of lime is an oxidation process; the chlorine itself, which is the active constituent of the bleaching powder, does not directly destroy the coloring-matter in the fiber. In the presence of water, however, the chlorine liberated in a nascent condition from the chloride of lime reacts with the formation of oxygen, and it is the latter which acts on the coloring matter.

Skein yarn may also be bleached by being linked together in the form of a long chain and run continuously through machines provided with squeeze rollers. Yarn in the form of prepared warps may also be bleached in a similar manner. There are also special machines for the bleaching of cotton slubbing and yarn in the form of cops and tubes, the yarn or slubbing being wound on perforated tubes and so arranged on the machine that the bleaching liquors are forced through the cotton either by means of vacuum suction or pumps.

Cloth bleaching is the principal method, however, for the bleaching of cotton. There are several methods of carrying out this form of bleaching depending on the ultimate use to which the goods are to be put. When the cloth is destined to be sold as white muslin the process is known as the *market bleach;* when the cloth is subsequently to be dyed with alizarin colors (especially red), a so-called *Turkey-red* or *bottom bleach* is given; whereas cloth intended for printing is given the *madder bleach.* These names are quite old in their application and are falling into disuse as characteristic terms. In bleaching for white goods for the market it is desirable to obtain a clear white color with a bluish tint, and the appearance of the goods also depends to a considerable degree on the finishing processes given the cloth after bleaching. The Turkey-red bleach is only for the purpose of providing a white bottom for dyed colors so that the latter will appear bright and clear. The bleaching required of print cloth is by far the most complete and thorough, as it is necessary to remove all impurities from the goods so as to leave the cotton not only white in color but also in the form of chemically pure cellulose so that the printing colors may be properly applied. A general outline of the various processes in this method of bleaching is as follows:

Marking. The cotton pieces as they come from the loom are stitched together and marked with a special ink capable of resisting the bleaching operations so they may be subsequently identified.

Singeing. The cloth is passed rapidly through a series of gas jets so

as to burn off the loose fibers and lint from the surface. The singeing may be done on one side only or on both sides as required. Instead of being passed through gas jets the cloth may be passed over curved copper plates heated to redness, or over a heated revolving copper roller. Singed cloth gives a clear even surface so that fine and delicate patterns may be sharply and clearly printed.

Gray Wash. This is a preliminary wetting out in water and has for its purpose the removal of much of the external dirt as well as the softening and removal of much of the sizing used on the warp yarns in weaving the cloth. This operation is frequently omitted.

Boiling Out. This is a similar operation to the boiling out of cotton yarn. It is usually conducted in large closed iron kiers provided with a suitable mechanism for the circulation of the liquor through the goods. The boiling is usually conducted under pressure (from 10 to 80 lbs.) for from six to eight hours. It was formerly the custom to give a first boiling with milk of lime (lime boil). The goods were passed through a solution of milk of lime and without squeezing were packed into the kier; sufficient water was next introduced and the kier boiled with superheated steam. The lime boil was considered necessary to decompose the fatty matters in the cotton with the formation of a lime soap, and also to convert the starch (or other dressing materials on the cloth) into a soluble form. Of late years, however, the lime boil is being dispensed with as a preliminary operation, and the boiling out is done in one operation with caustic soda. When the lime boil is used it is necessary to give a thorough washing to the goods and then to pass them through a weak bath of sulphuric acid (1° Tw.) known as the *gray sour*. This is for the purpose of dissolving out the lime compound in the fiber as well as any iron stains which may have formed in the kier. After the acid treatment another thorough washing process is required. After the gray sour the goods are given a second boiling in the kier with caustic soda; generally mixtures of caustic soda, soda ash, and rosin soap are employed, and from two to three boilings are given. These boilings remove all of the waxy and fatty matters and most of the pectin compounds in the fiber. The use of rosin was once considered essential to the perfect scouring of cotton for purposes of print cloth. At the present time, however, the tendency is to omit the the rosin boil; in fact, the boiling out is reduced to the single operation of treating in the kier with caustic soda solution.

Washing. After the boiling out, in whatever manner it may be conducted, the goods are very thoroughly washed in order to remove as far as possible all of the decomposed impurities and residual alkali. The washing is conducted in special forms of washing machines and well flushed with fresh water.

Chemicking. This is the general term given to the treatment with the solution of bleaching powder. The strength of the solution employed is usually 1½ to 2° Tw., and the liquor should be clear and free from

undissolved particles or sediment. The damp cloth is saturated with this chemic solution, passed through squeeze rolls, and then piled up and left exposed to the air for some hours. This allows the carbonic acid of the air to react with the bleach liquor with the formation of free hypochlorous acid which destroys the coloring matter present through its strong oxidizing action. Care must be had not to allow the oxidizing action to proceed too far or the cotton fiber itself will be attacked and weakened by the formation of oxycellulose. In some methods of bleaching, instead of exposing the cloth to the action of the air, it is steeped in the solution of bleaching powder for some hours, or the cloth is packed in suitable kiers and the chemic solution is circulated through it by means of pumps.

Souring. After treatment with the chemic solution the cloth contains a considerable amount of lime compounds and undecomposed chlorine derivatives. The souring, or treatment with a dilute solution of sulphuric acid 1° Tw., is for the purpose of removing or decomposing these compounds. The cotton also becomes much whiter in color after the treatment with acid, hence this process is known as the *white sour* (in contradistinction to the gray sour when a lime boil is used). Instead of using sulphuric acid for souring, hydrochloric acid is sometimes employed, as the lime salt with this latter acid is much more soluble; hence much easier to remove from the fiber. After souring a very thorough washing must be given the cloth in order to remove all salts and acid residue.

Finishing. The final operation in bleaching cotton cloth is to give it a finish suitable to the use for which it may be intended. In the case of a market bleach, the cloth must be tinted to a proper tone of bluish white and also be starched and calendered to give it a smooth and polished surface. Cloth intended for dyeing, of course, is not tinted, and receives its special finish after it is dyed. Print cloth is also not tinted, and it is finished in the printing operation.

Of late years a number of bleaching processes have been brought forward with the object of making the process shorter and more automatic. Special forms of kiers have been devised where the cloth is treated to all the operations with a minimum degree of handling. One such method which is being largely used is the so-called Mather-Thomson Process which uses an improved form of apparatus. In place of using solutions of chloride of lime, the chemic is sometimes prepared by the electrolysis of a solution of common salt. This furnishes a hypochlorite of sodium, but the bleaching efficiency is said to be much greater than a corresponding amount of bleaching powder solution. A similar solution can be prepared more economically and satisfactorily by the use of liquid chlorine. This product is employed in connection with soda ash.

Linen. This is next to cotton in importance as a vegetable textile fiber. It is obtained from the *bast* of the flax plant, *Linum usitatissimum*, and differs considerably from cotton in its structure and appearance.

The flax plant is grown largely for its fiber in Europe; Ireland and Russia being the chief producers. Though also grown extensively in other parts of the world, it is cultivated principally for its seed, which ultimately furnishes linseed oil. In preparing the fiber the entire plant is taken and put through a *rippling* machine for the purpose of removing the leaves, seeds, etc. The cleaned stalks are then subjected to a process known as *retting* for the purpose of decomposing the woody tissue and dissolving the resinous and gummy matters so that the free fiber may be obtained. Retting is essentially a fermentation process, and a number of different methods are employed. The two chief methods are: (1) steeping in stagnant water. The flax straw is tied into convenient bundles and laid down in pools of soft water. Fermentation rapidly sets in, and when the woody tissue has been decomposed, but before the fiber itself is attacked, the bundles are removed and spread out on the grass for a number of days, where they may be exposed to the combined action of sunlight and air. The pulpy stalks are then passed through special breaking and scutching machines for the purpose of breaking up and removing the decomposed matters and leaving the fiber free and clean. Flax produced in this manner has a rather dark grayish-brown color, as the coloring matters formed during the retting process are not removed. The majority of the Irish flax and some of the Russian flax is retted in this manner. (2) Steeping in fresh running water (in streams) is another method of retting by which most of the French and Belgium flax is made. The bundles of flax straw are submerged in the streams by means of crates. The fermentation proceeds more slowly than by the first method, but the coloring matters are removed by the running water, so the final product is much lighter in color, and the fiber is of a superior quality. Flax may also be retted by exposing the stalks for a number of weeks to the action of dew. There have also been a number of "improved" chemical methods proposed for the retting of flax, chiefly with the purpose of hastening the fermentation and obtaining a brighter and clearer fiber.

The linen fiber as it appears in trade is in the form of long, rather coarse, filaments of a silver or brownish color. These fibers consist of a number of comparatively small elongated cells cemented together by a glutinous intercellular substance. The individual fiber cells are about 1 to 2 ins. in length and from 12 to 25 μ[1] in diameter. The fiber is cylindrical with thick cell-walls and a narrow internal canal. Under the microscope the fiber shows the presence of peculiar cross-marks resembling joints or dislocations (see Fig. 326).

FIG. 326.—Linen Fiber.

In its chemical properties linen is very similar to cotton, but its cellulose

[1] The expression μ indicates the thousandth of a millimeter (0.001 mm.). It is a unit extensively employed for microscopic measurements.

is less pure owing to the intercellular substances present. The following is an average analysis showing the composition of linen:

Water	8.65–10.70%
Aqueous extract	3.65– 6.02
Fatty and waxy matters	2.39– 2.37
Intercellular matters	2.74– 9.41
Cellulose	82.57–71.50
Ash (mineral matter)	0.70– 1.32

Linen is bleached in the same general manner as cotton, but as the fibers are more or less disintegrated into the individual cells by the bleaching process, fully bleached linen is much weaker than raw linen. On this account, linen is generally only partially bleached. In its general characteristics linen is stronger than cotton but less elastic; it is a better conductor of heat, hence linen garments are colder than those of cotton. Linen also has a higher degree of luster than cotton.

Jute. This fiber is without doubt next in commercial and technical importance to linen. It is also a bast fiber obtained from the stalks of *Corchorus capsularis*, or Jew's mallow, growing in tropical and subtropical countries. The majority of the jute of commerce comes from India and the East Indian Islands. The fiber is prepared from the stalks by a simple retting in water, the fiber separating rather readily from the other tissues. As it appears in trade the fiber is from 4 to 7 ft. in length, usually of a yellowish brown color, though some qualities are of a silver-gray color. It has considerable luster and a high tensile strength. The cell-elements of the jute fiber are rather small, being about 1.5 to 5 mm. in length and 20 to 25 μ in diameter. The fiber is composed of a rather large number of these cell-elements cemented together. A cross-section of the fiber shows these cells to have a polygonal outline. The microscopic appearance of the jute fiber differs from that of linen in not exhibiting the peculiar jointed ridges running across the fiber.

In its chemical composition and properties, jute differs essentially from the other vegetable fibers. Instead of being composed of relatively pure cellulose it appears to consist almost altogether of a modified form of cellulose known as ligno-cellulose or bastose. This is shown by the fact that the jute fiber gives a yellow coloration when tested with iodin-sulphuric acid reagents, whereas ordinary cellulose gives a blue color. Owing to its different chemical composition, jute behaves quite differently with the various classes of dyestuffs, as it combines directly with both acid and basic dyes, whereas cotton and linen require mordants for these colors.

The Minor Vegetable Fibers. There are a number of vegetable fibers which are largely used for the manufacture of cordage, mats, etc., and which can scarcely be termed textile fibers in the sense of being utilized for woven fabrics. Hemp and sisal are the principal fibers used for cordage.

The former is a general name for a large number of commercial fibers of similar physical appearance and properties, and obtained from a number of different plants. Sisal is a fiber obtained from the leaf tissues of the *agave* and other similar plants. Ramie or China grass is a bast fiber obtained from species of the nettle plant. It is a fine white and very strong fiber which would be very valuable commercially except for the difficulty with which it is obtained from the plant and from the fact that the surface of the fiber is so smooth that it lacks cohesion in spinning.

Artificial Silk. This is a fiber which is attaining considerable commercial value. It is a cellulose fiber artificially prepared from suitable solutions of cellulose by forcing the liquid through fine orifices and coagulating the cellulose as it emerges in the form of a delicate thread. There are a number of methods at present used for the production of this fiber, among which the following are the most important: (1) Pyroxylin or chardonnet silk prepared from a solution of guncotton in a mixture of alcohol and ether; as the thread is formed the solvent is evaporated and the nitrated cellulose becomes coagulated into a continuous filament. This thread is subsequently denitrated by treatment with solutions of nitric acid, ferric chloride, and ammonium phosphate. (2) Cupra-ammonium silk is prepared from solutions of cellulose in the copper-ammonium sulphate solvent known as Schweitzer's reagent. The thread is coagulated and the metallic salts removed by a treatment with a solution of sulphuric acid. (3) Viscose silk is prepared from a solution of viscose or cellulose thiocarbonate, the thread being coagulated by passing through a solution of ammonium sulphate, and subsequently washed very thoroughly to remove the sulphur compounds that are formed in the decomposition of the viscose. These artificial silks resemble true silk very closely in general appearance, possessing even a higher luster than the latter. The fiber, however, is more wiry and harsh in nature, and its strength and durability is considerably below that of true silk. The strength of artificial silk is also greatly lessened when wetted with water. This fiber, however, has a large use in the manufacture of braids, dress trimmings, passementerie, and ornamental fabrics of various kinds where a high luster is especially desirable. Artificial silk is dyed in the same manner as cotton.

XXXVIII

DYESTUFFS AND THEIR APPLICATIONS

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Textile Coloring. Textile coloring may be defined as the process or combination of processes used to fix a color or colors uniformly, and more or less permanently, upon textile material. It includes both dyeing and printing.

Dyeing. The term dyeing is sometimes given almost as broad an interpretation as textile coloring, but to be specific, it should include only those processes in which the entire body of the material being colored, is immersed in the coloring bath, a greater or less period of the time required for the coloring.

Textile Printing. Textile printing is a process by means of which the coloring matters applied may be confined, by use of a printing machine, to certain portions of the material, thus producing a definite colored design. The necessary dyestuffs and chemicals are made into a paste, with starch, dextrine, and various gums, and applied to the cloth by means of copper rollers, one for each color, the cloth being finally subjected to special aging and drying processes. By this method it is possible to produce prints containing ten or more different colors.

By combined dyeing and printing many different and pleasing effects may be produced.

Staining. Staining is the term often applied to the process of coloring such materials as wood, bone, and ivory, and the coloring matter in this case is ordinarily applied with a brush.

The terms staining and dyeing are both applied to the coloring of leather, straw, paper, and feathers, their respective use depending somewhat upon the process used, but in most cases the term dyeing is more accurate.

Compounds Used by the Textile Colorist. The chemical compounds used by the textile colorist may be divided into two classes:

(1) Those which possess no coloring power, but which are instrumental in the fixation or development of coloring matters upon the fiber.

(2) Those which are true coloring matters.

First Class. Compounds Instrumental in the Fixation of Coloring Matters upon the Fiber, although possessing no Coloring Power Themselves. The compounds included under this heading are frequently spoken of as *fixing agents*, but when used in this broad and indefinite sense, the term frequently leads to confusion rather than to enlightenment. In order to eliminate this confusion as far as possible, we will classify the most important compounds coming under this class as follows:

(1) Mordants: (*a*) Metallic. (*b*) Non-metallic. (*c*) Acid.
(2) Mordanting assistants.
(3) Chemical fixing agents.
(4) Mechanical fixing agents.
(5) Developing agents.
(6) Leveling agents.
(7) Dyeing assistants.

Mordants. Mordants in general may be defined as substances capable of uniting with certain dyestuffs to form insoluble colored compounds which under the proper conditions may be more or less permanently fixed upon textile material. They may be subdivided as *metallic, non-metallic,* and *acid mordants.*

Metallic Mordants. Metallic mordants are substances, usually metallic oxides or hydroxides which are capable of uniting with certain dyestuffs, known as mordant dyestuffs, to form insoluble colored compounds which for the most part are known as *color lakes.*

Non-metallic Mordants. The only non-metallic mordant of importance, and this of only minor importance, is sulphur. Sulphur is sometimes used as a mordant when applying certain basic colors, e.g., malachite green upon wool.

Acid Mordants. Tannic acid and various substances rich in this acid, such as sumac, gall nuts, and various bark extracts, and less frequently various fatty acids, such as oleic and stearic acids, and Turkey red oil, are the only acid mordants of importance. Of these acid mordants tannic acid and its related compounds are the only ones commonly used, and these chiefly in the application of the basic colors to cotton material. The acid mordants are of minor importance as compared with the metallic mordants.

Mordanting Principles. As often applied, the term "mordant" indicates the soluble metallic salt used to produce the mordant, but in the proper sense the mordant is that substance, which in direct combination with the dyestuffs, forms the color lake. In order to avoid this confusion, we will designate the compound used to produce the mordant as the *mordanting principle.* Thus in one of the most common wool mordanting processes the soluble potassium dichromate is the mordanting principle, and the oxide of chromium ultimately fixed upon the fiber is the true mordant.

Mordanting Assistants. Mordanting assistants are compounds such as tartar, lactic acid, and sulphuric acid used in conjunction with the mordanting principles to bring about a gradual decomposition of the latter, and assist in producing a uniform deposition of the actual mordant upon and within the textile material.

Mordanting Process. The mordanting process is the operation whereby various mordants are precipitated and so deposited upon textile material that they may be subsequently united with mordant dyestuffs *in situ* to form insoluble color lakes. Occasionally, in special cases, the dyestuffs may be applied at the same time or even previous to the mordant.

Chemical Fixing Agents. Under the heading of chemical fixing agents we will include:

First. Those substances which are instrumental in the fixation of various mordants upon textile material by uniting chemically with such mordants and holding them upon the fiber until the proper dyestuffs may be given an opportunity to unite with them. Examples: The various antimony compounds used to fix tannic acid upon cotton fiber. Various tannin compounds used to hold iron upon the fiber as the insoluble tannate of iron when the latter is to act as a mordant with logwood or other mordant dyestuffs.

Second. Those substances which cause the actual precipitation of the mordant usually by the double decomposition of the mordanting principle. Example: When cotton material saturated with nitrate of iron is passed through a solution of sodium carbonate, the basic carbonate and oxide of iron is precipitated upon the fiber, and sufficiently fixed thereon to act as a mordant.

Mechanical Fixing Agents. These are substances (such as albumen) capable of holding pigments, permanently, upon the fiber, or certain gums and starches capable of holding dyestuffs and other substances upon the fiber a sufficient length of time to permit some desirable reaction taking place. Their action is purely mechanical.

Developing Agents. The term, developing agents is applied to organic compounds which in combination with some other organic compound already deposited upon the fiber will develop a colored compound, or if united with a dyestuff already upon the fiber will form a new coloring matter possessing a more desirable or a faster color. Examples: Beta-naphthol upon the fiber, when combined with diazotized para-nitro aniline (developing agent) will produce para red. Primuline, a yellow dyestuff, when diazotized upon the fiber by treatment with nitrous acid and then combined with beta-naphthol (developing agent) produces a very bright red coloring matter.

Leveling Agents. Leveling agents are compounds added to the dye-bath in conjunction with certain dyestuffs to assist in bringing about the level or even deposition of the latter. Example: Glauber's salt used in conjunction with the direct cotton colors.

Dyeing Assistants. Dyeing assistants are compounds which added to the dye-bath, facilitate the dyeing process and are beneficial in one way or another. Examples: Sulphuric acid and Glauber's salt in the dyeing of acid colors.

Application of Metallic Mordants. True mordant dyestuffs can only be applied in conjunction with metallic mordants. The mordanting process is therefore of great importance, the mordant playing almost as necessary a part in the application of a mordant color as does the dyestuff itself. Of all the metals, only a few, namely chromium, iron, aluminium, copper and tin unite with mordant dyestuffs to form valuable color lakes. On account of its general applicability chromium is most frequently used. Iron and copper produce the most permanent, while aluminium and tin produce the brightest color lakes.

Mordanting of Wool. Wool has a natural affinity for certain compounds and this facilitates the mordanting process to a marked degree. When in dilute solution mordanting principles, often in a highly dissociated condition, are aided in their decomposition by this natural attraction of wool fiber, and as a result various metallic compounds (usually oxides or hydroxides) are slowly deposited upon the fiber. This process takes place most completely in a boiling bath and in the presence of some secondary soluble compound which has already been described as a mordanting assistant.

Chromium compounds are depended upon, almost entirely, in applying mordant dyestuffs upon wool, and potassium dichromate is the most important mordanting principle for this purpose. The process most frequently used consists in boiling the wool material in a dilute solution of potassium dichromate in the presence of either tartar or lactic acid the latter acting as mordanting principles. The boiling should be continued for about one to one and one-half hours in order to secure the most complete decomposition of the mordanting principle, and fixation of the mordant upon the fiber.

Mordanting of Silk. Silk, like wool, possesses a marked affinity for metallic oxides and hydroxides, and for this reason may be readily mordanted. The process consists in steeping the silk in a concentrated solution of the proper mordanting principle, such as the sulphate, chloride or acetate of iron, chromium, aluminium or tin, usually in a slightly basic condition, and then thoroughly washing with a large volume of water. This process may be repeated several times depending upon the depth of color to be obtained upon dyeing.

Mordanting of Cotton. The mordanting of cotton is more difficult than that of either wool or silk owing to the entire lack of natural attraction of cotton for metallic salts and oxides. The methods of cotton mordanting are numerous, but may be grouped under four general headings:

(1) Combined padding, aging, and dunging process.
(2) Combined printing, aging, and dunging process.
(3) Direct chemical precipitation upon the fiber.
(4) Steam printing.

In the first method, the cloth is evenly saturated (padded) with a solution of some mordanting principle, usually an acetate of chromium, iron, or aluminium. It is then subjected to a hot moist atmosphere for a number of hours (aging) which brings about a slow decomposition of the acetate with fixation of metallic oxide upon the fiber, and liberation of acetic acid. The fixation of the mordant, and neutralization of the free acid present is brought about by the dunging process which consists in thoroughly treating the aged material in a bath made up with such substances as phosphates, silicates, and carbonates of potassium, sodium, ammonium, and calcium. Sodium arsenate is a valuable fixing agent for this purpose but its use has been largely discontinued owing to the poisonous nature of the arsenic.

The second method differs from the first only in that the mordanting principle is printed upon the fabric rather than padded.

The third method consists in the direct chemical precipitation of the mordant upon the fiber. In this method the material is first padded with the mordanting principle and then passed through a bath containing the precipitant.

In steam printing the mordanting principle and mordant dyestuff are mixed together with the proper thickening agents and then printed upon the cloth. Upon steaming, the mordanting principle decomposes and forms the mordant which unites with the coloring matter *in situ.*

Second Class. Coloring Matters and Dyestuffs. In general, a coloring matter is a substance which if properly used will impart a characteristic color to some other substance. By common usage the term dyestuff is almost synonymous with that of coloring matter, particularly as applied to textile material.

Classification of the Dyestuffs. The earliest classification of dyestuffs was made by Bancroft who divided them into two classes *substantive* and *adjective.* He designated as substantive dyestuffs those capable of producing a fully developed color upon textile material without the necessary assistance of any other combining substance, and as adjective dyestuffs those requiring an intermediate combining substance (*called a mordant*) to satisfactorily fix and fully develop the color. This grouping is still in use, but during recent years, the tendency has been to use the term, *direct color* instead of substantive, and *mordant color* instead of adjective. In general the classification holds true; but there are instances where dyestuffs are substantive toward one fiber, but adjective toward another. This is well illustrated by the basic colors which will dye wool directly but require a mordant upon cotton.

The *classification which divides the dyestuffs according to their origin* is of broader application. It recognizes three groups and is as follows:

(1) *Natural Organic Dyestuffs.* Including (*a*) *Vegetable;* (*b*) *Animal.*
(2) *Mineral Dyestuffs.*
(3) *Artificial Organic Dyestuffs.*

Though the various subdivisions of this classification, particularly of the artificial organic dyestuffs, are numerous and varied in the character of the dyestuffs they include, this general classification has the advantage of conciseness, and one class does not overlap another.

The natural organic dyestuffs include such coloring matters as logwood, indigo, fustic, cutch, and cochineal.

The mineral coloring matters include Prussian blue, chrome yellow, iron buff and a number of other inorganic pigments.

The artificial organic dyestuffs are the most important and this class may be divided into twenty or more important sub-classes. They include all of the so-called coal-tar dyes, such as magenta, benzo-purpurine, acid violet, tartrazine, and the alizarines.

Natural Organic Dyestuffs. For convenience we shall subdivide the natural organic dyestuffs as follows:

(1) Indigo and related compounds.
(2) Logwood.
(3) Natural dyestuffs producing shades of a red character.
(4) Natural dyestuffs producing shades of a yellow to brown character.

Indigo. Indigo blue or indigotin occurs in many plants, chiefly those of the genus *Indigofera*, the *Indigofera tinctoria* yielding the largest quantity. The Indigofera thrive only in tropical climates, and for several hundred years the cultivation of the indigo plant was one of the chief industries of Southern Asia, particularly India and Java. The introduction of the artificial indigo however has dealt a severe blow to the natural indigo industry, particularly during the past five years, and the synthetic indigo now seems likely to entirely replace the older vegetable product.

The indigo plant is herbaceous in character, grows 3 or 4 ft. high, and with a stem about ¼ in. in diameter.

Indigo blue, or *indigotin* as it is known chemically, does not exist as such in the plant, but is developed through the indirect decomposition of a glucoside known as indican. When the leaves and stems are steeped in water and allowed to ferment, a clear yellow liquid results which contains the indigo as the soluble indigo white. When this liquor is violently agitated, so as to expose all parts to the action of the oxygen of the air, the soluble indigo white is converted into the insoluble indigo blue. This

is allowed to settle, pressed into cakes, and when dry is ready for the market.

Chemistry of Indigo Dyeing. Indigo differs from the majority of dyestuffs in that it is insoluble in all of the reagents which the dyer can employ practically, but nature has fortunately given it a property which renders its application comparatively simple. When reduced in an alkaline bath, it is easily converted into the soluble indigo white as follows:

$$\underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2}+2H=\underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2}.$$

Upon even the mildest oxidation, indigo white passes back to indigo blue as follows:

$$\underset{\text{Indigo white}}{C_{16}H_{12}N_2O_2}+O=\underset{\text{Indigo blue}}{C_{16}H_{10}N_2O_2}+H_2O.$$

Indigo white being readily soluble in alkaline water solution, and this solution being easily absorbed by both animal and vegetable fibers, the process of application becomes comparatively simple. Upon exposure of the saturated fiber to the air, the indigo white is oxidized almost immediately to the insoluble indigo blue, which is rapidly precipitated upon and within the pores of the fiber to as great a depth as the indigo white solution has penetrated. The alkaline bath of indigo white is commonly called an *indigo vat*, and this process of coloring is usually spoken of as *vat dyeing*.

Application of Indigo. Indigo is extensively used for the dyeing of cotton and wool, but seldom for silk.

Three forms of indigo vats are chiefly depended upon at the present time.

(1) Fermentation Vats.
(2) Zinc lime vats.
(3) Hydrosulphite vats.

These vats all involve the principle of reducing finely ground indigo to indigo white, and differ only in the methods used to bring about this reduction.

The *fermentation vat* is the oldest, but is still largely depended upon in wool dyeing, although never used for cotton dyeing. The reduction in this case is brought about by the fermentation of various organic substances such as bran, woad, molasses, and madder in an alkaline solution.

The *zinc lime vat* has been used largely for cotton dyeing, but not for wool dyeing. The reduction in this case is brought about by the action of zinc powder upon water in the presence of an alkali, that alkali being calcium hydroxide. The reaction may be represented by the following equation.

$$Zn+2H_2O=Zn(OH)_2+2H.$$

The *hydrosulphite vat* is the most recent of the indigo reduction vats, and has largely replaced the fermentation vat for wool dyeing, and the zinc lime vat for cotton dyeing. In this vat the reduction is brought about by means of a sodium hydrosulphite solution, which is commonly prepared just before use by the action of zinc dust upon sodium bisulphite solution. The reactions may be represented by the following equations:

$$2NaHSO_3+Zn=Na_2S_2O_4+Zn(OH)_2$$

$$Na_2S_2O_4+2H_2O=2NaHSO_3+2H.$$

The application of indigo to *cotton and wool* differs chiefly in the fact that it is more difficult to penetrate wool than cotton with the indigo white solution and thus a longer period of immersion and a somewhat higher temperature is required.

Cotton requires an immersion of only a minute at ordinary temperature, unless the material is heavy, while wool requires from twenty minutes to an hour at a temperature of 120° F.

Indigo Extracts. These are prepared by the action of concentrated sulphuric acid upon indigo blue. The resulting compounds are the indigotin sulpho acids, which are freely soluble in water, and may be easily applied to wool in an acid bath. They dye wool a brighter blue than ordinary indigo, but unfortunately the dyeings produced are extremely fugitive to light, whereas vat indigo on wool produces one of the fastest blues known. The use of the former is very much restricted for this reason. The indigo extracts are of no value for cotton dyeing.

Logwood. Logwood is the product of a large and rapidly growing tree known botanically as the *Hæmatoxylin campechianum.* It is a native of Central America and the adjacent islands, Jamaica being one of the chief centers of the logwood industry. Raw logwood, as the name implies, comes in the form of rough logs, which are ground or rasped into small chips. It may be used in this latter form after it has been properly aged, but during recent years it has been more frequently put upon the market in the more concentrated form of an extract.

Chemistry of Logwood Coloring. Careful examination of freshly cut logwood chips reveals the presence of a yellowish-crystalline compound having the empirical formula $C_{16}H_{14}O_6$ and to which the name *hæmatoxylin* has been assigned.

When exposed to the air hæmatoxylin, especially in the presence of an alkali, rapidly oxidizes to a reddish-brown substance known as *hæmatein* and having the empirical formula $C_{16}H_{12}O_6$. Hæmatein is the active coloring matter of logwood. Upon further oxidation it passes into a resinous brown substance which is of no value for coloring purposes.

Logwood is in every sense of the word a mordant dyestuff, a metallic mordant being required to satisfactorily fix the dyestuff upon any textile fiber. During the dyeing process the hæmatein of the logwood unites

with the mordant to form an insoluble metallic organic compound or color lake, which becomes fixed upon the fiber.

The chief metals entering into these color lakes are chromium, iron, aluminium, and copper. Logwood is commonly classified as a black dyestuff, and is used chiefly for the production of blacks, but more strictly speaking, it is a blue dyestuff, for with both aluminium and chromium, it produces blue dyeings and although with iron the shade produced approaches black, it is customary to add a small amount of some yellow dyestuff to produce a satisfactory black.

Aging of Logwood. In general, logwood, when ready for the dyer, should contain a high percentage of hæmatein, but little unoxidized hæmatoxylin, and none of the resinous brown oxidation product already mentioned.

In order that this ideal condition may be approached as nearly as possible, logwood must be aged.

Logwood chips are commonly aged as follows;

After having been made into a large pile several feet in depth, the chips are well moistened with water, and then worked over with wooden shovels, every portion of the pile being thus brought in contact with the air. This is continued for a period of from three or four days to two weeks, depending largely upon atmospheric conditions. After some experience one can tell, from the appearance of the chips when the right stage of oxidation is reached. The chips are then stored in such a way as to be exposed as little as possible to the oxidizing influence of the air.

When aged logwood is known to contain much hæmatoxylin, and consequently incompletely aged, the aging may be continued to a certain extent during the dyeing process by adding some oxidizing agent or using an oqidizing mordant, e.g., chromium in the CrO_3 form.

Logwood Liquor. Logwood liquo is a decoction o ogwood made by extracting aged logwood chips with water. It usually has a strength of 15° Tw. (Sp.gr. 1.075) and as it does not keep well is on'y made as required for use.

Logwood Extracts. At the present time, logwood is most frequently put upon the market in the extract form. Logwood extracts are made by evaporating logwood liquor in vacuum pans until it reaches a sp.gr. of 1.25 or 50° Tw., or it may be carried to dryness to produce the solid extracts.

These solid extracts are prepared by patented processes. They vary somewhat in strength and chemical character, and are frequently designated as *hæmatine crystals.*

Application of Logwood. Logwood is still used in *wool dyeing* on account of its cheapness, and because the characteristic bloomy blue black which it gives is difficult to produce at as low a cost with coal-tar coloring matters. In wool dyeing, logwood is chiefly used in conjunction with a chromium mordant, a small amount of some yellow dyestuff,

frequently fustic, being combined with it, to overcome the pronounced bluish cast which would otherwise result.

One dip logwood blacks are prepared by using in conjunction with logwood some mordanting principle, and a sufficient quantity of an acid, usually oxalic, to prevent too rapid precipitation of the color lake. A mixture frequent y used for this purpose consists of logwood extract, ferrous sulphate, copper sulphate, and oxalic acid.

The use of logwood upon *cotton* has greatly diminished during recent years logwood blacks having been largely replaced by aniline black, sulphur blacks, and certain direct cotton blacks. When used upon cotton it is most frequently applied in conjunction with an iron mordant either alone or in combination with a copper mordant.

Logwood is extensively used for the production of blacks upon *silk*. Iron mordants are depended upon almost entirely for this purpose and tin mordants occasionally. The process usually consists in alternately treating the silk with some tannin material, and an iron or a tin compound until the silk is thoroughly filled with the metallic tannate. The silk thus mordanted is then dyed in a logwood bath. By using tin compounds in conjunction with acetate of iron it is possible to weight bla k dyed silk as much as 300 per cent of its original weight.

Soluble Red Woods. Brazil wood, peach wood, Japan wood, and Lima wood are the principal soluble red woods. They are all mordant colors, and may be applied to mordanted cotton or wool by boiling in a plain bath of the extracted color.

Insoluble Red Woods. These include barwood, Saunders wood, and camwood. On account of the insolubility of the coloring matters which they contain, the ground or rasped chips of wood must be added directly to the dye bath. They are all mordant colors. The red woods have been replaced by coal tar colors which give more permanent and clearer dyeings at a lower cost.

Madder. Madder root, which was known to the ancients, was for many hundreds of years the most important of the red natural coloring matters and was used chiefly in conjunction with Turkey reds. The active coloring principle of madder is alizarine $C_{14}H_8O_2$, and the discovery in 1868 by Graebe and Liebermann that alizarine could be cheaply made from coal tar derivatives, soon led to the abandonment of madder as a coloring matter except in the Oriental countries where it is native.

Cochineal. Cochineal is a red mordant coloring matter obtained from the dried body of an insect, which is native of Mexico and Central America. In the past cochineal was extensively used for the production of scarlets and crimsons on wool in conjunction with tin and aluminium mordants. Like most of the other natural colors, cochineal has been superseded by the artificial dyestuffs.

Other red natural dyestuffs worthy of mention are kermes, and lac dye, which are similar to cochineal in origin, though of less importance;

also orchil and cudbear bluish red coloring matters which like litmus are derived from certain rock mosses or lichens.

Natural Dyestuffs of a Yellow to Brown Color. *The yellow natural dyestuffs* include a number of vegetable dyestuffs which vary between yellow and brown. Fustic, quercitron bark, Persian berries, turmeric, weld, and cutch are the most important.

Fustic or Cuba Wood. Fustic or Cuba wood is the most important of the yellow dyewoods and is still used to some extent in wool dyeing chiefly in combination with logwood. It is a mordant dyestuff being used with chromium and aluminium mordants. It is sold in the form of ground wood, but more frequently as an extract.

Quercitron Bark. Quercitron bark is obtained from the bark of a species of oak which grows in the Middle and Southern States. It is a mordant color and gives brighter yellows than fustic. Its use is limited at the present time.

Persian Berries. Persian berries is the name applied to the berries of the buck-thorn. In the extract form it is used to a limited extent in calico printing.

Turmeric. Tumeric is the ground root of a plant which grows in Asia. It dyes cotton, wool, and silk bright shades of yellow which are extremely fugitive to light and washing.

Cutch or Gambia. Cutch or gambia, a coloring matter rich in tannin, is extracted from the nuts and tender portions of various forms of acacia trees growing chiefly in India. It is used chiefly for the production of browns upon cotton also as a tannin material in silk dyeing.

Mineral Dyestuffs. The mineral dyestuffs as a class are of minor importance in the textile industry. Various mineral pigments are sometimes used in calico printing, but in the actual dyeing process the only mineral dyes of any importance are Prussian blue, chrome yellow, chrome green, iron buff, and khaki.

Prussian Blue. Prussian blue may be produced upon textile material by one of two methods. The first consists of mordanting the material with iron oxide, and then boiling in a solution of potassium ferrocyanide. The second method makes use of the fact that both the ferro and ferri cyanides of potassium decompose when boiled in an acid solution and from such a boiling solution Prussian blue is absorbed by textile material. The first process is used chiefly with cotton while the second is better adapted to wool dyeing.

Chrome Yellow. Chrome yellow is the yellow lead chromate which may be precipitated upon the fiber by alternate treatments with solutions of some soluble lead salt and a chromate.

Chrome Green. Chrome green is a basic oxide of chromium precipitated upon the fiber by the reaction of some soluble chromium salt with an alkali.

Iron Buff. Iron buff is a ferric oxide precipitated upon the fiber by the reaction of some soluble iron salt with an alkali.

Khaki. Khaki is a yellowish drab color produced by the precipitation upon the fiber of a combination of ferric oxide and basic chromium oxide. Khaki when properly dyed produces an extremely fast color.

Artificial Organic Dyestuffs. The natural dyestuffs were depended upon almost wholly until the discovery of mauve by Perkin in 1856. Mauve was the first of the so-called coal-tar dyes, or better artificial organic dyestuffs. Its discovery was followed by that of many similar dyestuffs, and a new era soon began in the textile coloring industry. To-day several hundred entirely different dyestuffs of this class are at the disposal of the textile colorist and from them we can select dyes which will answer almost every requirement of shade and fastness.

Classification of the Artificial Organic Dyestuffs. The artificial organic dyestuffs may be classified according to their chemical derivation, their composition, or in respect to the characteristic color forming groups which they contain. While these classifications prove very satisfactory for the color manufacturing chemist, they prove of little or no value to the practical textile colorist. Another classification which groups them according to their action toward the various textile fibers is by far the most practical and valuable for the student of textile coloring, and will be followed. It recognizes ten classes of coloring matters:

(1) Basic colors.
(2) Phthalic anhydride colors.
(3) Acid colors.
(4) Direct cotton colors.
(5) Sulphur colors.
(6) Mordant colors.
(7) Mordant acid colors.
(8) Insoluble azo colors. Produced directly upon the fiber.
(9) Reducible vat colors.
(10) Miscellaneous colors.

Basic Colors. Chemically the basic dyestuffs belong to the class of compounds known as substituted ammonias or amines. Like ammonia they are basic in character and hence the name.

The basic colors have a direct affinity for wool and silk, but no direct affinity for cotton and can only be applied to the latter fiber in conjunction with some acid mordant, usually tannic acid.

Application of Basic Colors to Wool. Although the basic colors have a direct affinity for wool, they are not extensively used in wool dyeing, for in most cases the acid colors are more desirable. When applied to wool it is customary to boil the material in a bath made up with the required quantity of dyestuff, sufficient acetic acid to render the bath

distinctly acid, and Glauber's salt equal to the per cent of the weight of material being dyed.

Application of Basic Colors to Silk. The basic colors have a direct affinity for silk, and are extensively used for dyeing this fiber when bright rather than fast colors are desired. The dye-bath is made up with 25 per cent "boiled off liquor"[1] and the remainder with water to which is added the required quantity of dyestuff and sufficient sulphuric, acetic, or tartaric acids to render the bath slightly acid. The silk material is entered at 100° F., the temperature of the bath then raised to 140° F., the material worked at this temperature for a few minutes, and the bath finally raised to a boiling temperature.

With dyestuffs which go on the fiber unevenly it is advisable to lift the silk material from the bath while the temperature is being raised.

Application of the Basic Colors to Cotton. Although the basic colors have no direct affinity for cotton, it is for the dyeing and printing of this fiber that the basic colors find their most extensive application. Before dyeing cotton material it must first be impregnated with tannic acid, and this fixed upon the fiber as an insoluble metallic tannate usually of antimony. When such a tannin mordanted cotton material is dyed in a bath containing a basic color, an insoluble combination of the dyestuff, tannic acid, and antimony results which becomes fixed upon the fiber. In calico printing the basic color and tannic acid are mixed together in the printing paste and chemical combination between the two is brought about by a subsequent steaming process. More thorough fixation of color may be obtained by after-treating the printed and steamed cloth with some soluble antimony compound usually tartar emetic.

Characteristic Properties of the Basic Colors. The basic colors are characterized by their great brilliancy and high coloring power. Their fastness to light is by no means satisfactory, but their fastness to washing in most cases is very good.

The Phthalic Anhydride Colors. The phthalic anhydride colors are so called because they are directly related to this compound. They include the eosines and rhodamines, and are extensively used for the production of bright pinks, particularly in silk dyeing, and less frequently in wool dyeing. They are not used to any great extent in cotton dyeing, although sometimes used in cotton printing.

Application to Wool. The phthalic anhydride colors are applied to wool in conjunction with alum, potassium bitartrate, and acetic acid.

Application to Silk. These colors are applied similarly to basic colors.

Application to Cotton. In calico printing the phthalic anhydride colors are applied in a similar manner to basic colors, or in conjunction with aluminium acetate.

[1] Preliminary to dyeing silk is subjected to the "boiling off" or "degumming process." The liquor resulting from this operation is known as "boiled off liquor."

Characteristic Properties. The phthalic anhydride colors are characterized by their remarkable brilliancy.

Acid Colors. The acid colors are so called on account of their acid character, and furthermore because they dye wool so readily in an acid bath. They are of great importance in wool dyeing, about 75 per cent of all wool dyeing being accomplished at the present time by their use. The acid colors are also extensively used in silk dyeing, but are of no importance in cotton dyeing.

From a chemical point of view the acid colors may be subdivided according to their composition into three classes: (1) Those which are nitro compounds, i.e., those containing the nitro or NO_2 group. (2) The sulphonated basic colors, i.e., those made by treating basic colors with concentrated sulphuric acid, and thereby introducing the sulphonic acid or HSO_3 group. (3) Those which are azo colors, i.e., those containing the azo or $-N=N-$ group. The dyestuffs of the third group are the most numerous and most valuable of the acid colors.

Application to Wool. The acid dyestuffs, almost without exception, are absorbed readily by wool in an acid bath and the dyeing process is comparatively simple. The dyebath is prepared with the required quantity of dyestuff, Glauber's salt equal to 15 per cent, and sulphuric acid equal to 3 to 5 per cent of the weight of the material being dyed. Instead of this mixture of Glauber's salt and sulphuric acid, a corresponding amount of sodium bisulphate may be used. The material is entered at a temperature of about 140° F., brought slowly to a boil, and dyed at a boiling temperature for three-quarters of an hour.

Application to Silk. In silk dyeing the proper quantity of dyestuff is added to a bath, made up with " boiled off liquor," and water to which has been added sufficient sulphuric acid to render the bath decidedly acid. The dyeing is begun at 100 to 125° F., and the bath slowly raised to 200° F., but no higher.

Application to Cotton. The acid dyestuffs have no affinity for cotton, and although occasionally used for special purposes they need not be considered in this respect.

Properties of Acid Dyestuffs. The number of the acid dyestuffs is so great and their properties so varied that it is difficult to describe definite properties that will apply to all.

Most of the acid colors are easily soluble in water, and, from an acidified water solution, animal fibers rapidly, and in many cases completely, absorb the dyestuff. The vegetable fibers in general have no direct affinity for the acid colors, jute, however, as an exception, has a slight affinity for a few special colors.

Direct Cotton Colors. The direct cotton colors, as their class name indicates, have a direct affinity for cotton. All vegetable fibers readily absorb the direct cotton colors from their simple water solution, but for practical results it is advisable to make certain other additions to the dye

bath. The direct cotton colors also dye the animal fibers directly but in most cases acid colors are preferred. The direct cotton colors having a direct affinity for both animal and vegetable fibers find extensive application in the dyeing of union material composed of cotton and wool, or cotton and silk.

Application to Cotton. The direct cotton colors are usually applied to cotton material by boiling for one hour in a dye bath made up with the necessary quantity of color, and Glauber's salt or common salt to the extent of 10 to 30 per cent of the weight of material being dyed. In some cases it is advisable to add from 1 to 3 per cent of soda ash, the quantity added varying with the depth of the color to be produced. In the dyeing of delicate tints, and with material which is difficult to penetrate, soap is sometimes added to the bath, and sodium phosphate used instead of Glauber's and common salts. It is always advisable to keep the bath as short, i.e., as concentrated, as possible, when applying these colors to cotton. An after-treatment with copper sulphate or potassium dichromate solution renders certain of the direct cotton colors somewhat faster to light.

Application to Wool. Wool may be dyed with most of the direct cotton colors in a neutral bath with or without the addition of Glauber's salt or common salt.

In some cases it is advisable to add a little acetic acid, but the addition of too much acid causes the dyestuff to go upon the fiber unevenly.

Application to Silk. The direct cotton colors are applied to silk in much the same manner as to wool. The addition of " boiled off liquor " is an advantage.

Application to Cotton and Wool Union Material. The direct cotton colors having a direct affinity for both cotton and wool are extensively used in the dyeing of union goods. By the choice of proper dyestuffs, and regulation of process, chiefly through variation of temperature, almost any color can be produced upon such material in one bath.

Properties of the Direct Cotton Colors. The direct cotton colors vary greatly in fastness. In general, they are not fast to washing when applied to cotton although much faster in this respect upon wool. Many of the reds are extremely sensitive to acid.

The property known as " bleeding " is one of the valuable as well as one of the detrimental characteristics of the direct cotton colors.

This property is well illustrated by the following experiment: Take a beaker of water and introduce into it a skein of yarn dyed with a direct cotton color and a skein of undyed yarn. Boil for an hour, when it will be found, in many cases, difficult to distinguish one skein from the other. The color has run or " bled " from the dyed skein and been taken up by the undyed.

This property is valuable since it tends to produce very level dyeings, and also to correct unevenness. On the other hand it is detrimental as

it prevents the use of the direct cotton colors for coloring of ginghams and in calico printing.

The direct cotton colors are, as a rule, readily soluble in water.

Sulphur Colors. The sulphur or sulphide colors, as they are frequently called, are in many respects similar to the direct cotton colors, but differ so entirely in many other respects that they are grouped by themselves. In recent years they have become an important factor in cotton dyeing, on account of the fastness of the dyeings they produce, and they are now extensively used for the production of fast blacks, blues, browns, and compound shades upon cotton.

They are called sulphur colors for three reasons: In the first place, sulphur is a constituent of all of the dyestuffs of this class; sulphur and sodium sulphide are largely used in their manufacture; and finally, sodium sulphide is almost without exception a necessary constituent of the dye-bath during their application.

Application of the Sulphur Colors. The sulphur colors are only used in the dyeing of vegetable fibers, the strongly alkaline sodium sulphide bath which must be used to hold the color in solution prohibiting their use with animal fibers. In general they are applied in a bath made up as follows: Dyestuff from 1 to 20 per cent of the weight of the material, sodium sulphide one to four times the weight of dyestuff, soda ash 5 to 10 per cent, and Glauber's or common salt 20 to 50 per cent of the weight of material being dyed. The material to be dyed is entered at or just below the boil, and dyed at this temperature for one hour. It is advisable to keep the textile material below the surface of the liquor as much as possible.

Properties of the Sulphur Colors. The most valuable property of the sulphur colors is their fastness to light, washing, and acids. Their fastness to chlorine and bleaching, however, is in most cases, not good.

Nearly all of the sulphur colors are insoluble in water, but dissolve readily in a solution of sodium sulphide. Copper vessels must not be used for their solution, as the sulphide present rapidly acts upon the copper coating it with the black copper sulphide.

The shades produced by the sulphur colors are mostly of a dull character, and blacks, browns, dark blues, dark greens and dull yellows; also various compound shades of these, such as drabs, slates, olives, and grays predominate. Sulphur yellows and greens as a rule do not equal the other sulphur colors in fastness. As yet no bright sulphur reds have been prepared.

Artificial Mordant Colors. The true mordant dyestuffs included under this heading cannot be permanently fixed upon cotton, wool or silk, except in conjunction with some metallic mordant. The nature of these metallic mordants and the methods of their formation upon textile material have already been described (see page 751). They are usually fixed upon the textile material as insoluble oxides or hydroxides of chromium,

aluminium, and iron, and less frequently tin and copper. During the dyeing process which follows the mordanting, the mordant dyestuffs, which contain either hydroxyl (OH) or carboxyl (COOH) groups in their composition, react with the mordants in much the same manner as acids react with bases, the result being the formation of insoluble metallic organic compounds of a salt-like character which are known as *color lakes.* This reaction taking place *in situ* and the color lake is thus fixed upon and within the fiber.

Application to Wool. The material which has already been mordanted (see page 752) is thoroughly washed and then dyed in a bath made up with the necessary quantity of dyestuff, and acetic acid. The latter is added to counteract any hardness or alkalinity of the water, and should be slightly in excess.

The dyebath should be at ordinary temperature when the material is entered, but the temperature should be slowly raised to a boil, and the dyeing continued at a boiling temperature for one and one-half hours. This prolonged boiling is necessary in order that complete chemical reaction may take place between mordant and dyestuff.

Application to Cotton. Cotton material mordanted by one of the methods already described may be dyed by simply boiling in a bath containing the mordant dyestuff, but it is more often the case that mordant dyestuffs are applied to cotton in conjunction with some mordanting principle by the steam printing process. (See page 750.)

Application to Silk. The mordant dyestuffs may be applied to mordanted silk but are seldom used for this fiber unless extreme fastness to soap and washing is desired.

Properties of Mordant Dyestuffs. While most of the artificial dyestuffs are soluble in water and sold in a powdered condition the mordant dyestuffs are the exception being nearly all insoluble in water and sold as liquid pastes which usually contain 20 per cent of coloring matter and 80 per cent of water. Alizarine is the most important of the mordant dyestuffs, and many of the other dyestuffs of this class are direct derivatives of alizarine. For this reason the mordant dyestuffs as a group are sometimes designated as the "alizarines." The mordant dyestuffs are characterized by their great fastness both to light and washing as well as all of the common color destroying agencies.

Mordant Acid Colors. The dyestuffs of the group known as the mordant acid colors are intermediate in general character between the acid dyestuffs and the mordant dyestuffs. They resemble acid colors in a general way, dyeing wool directly in an acid bath, but at the same time resemble the mordant colors, in that they may be applied, to advantage, in conjunction with metallic mordants.

During recent years, the number of mordant acid colors has greatly increased, and at the present time they are receiving much attention in wool dyeing, having replaced the mordant colors to a certain extent.

Their popularity lies in the ease with which they may be applied, and the fact that an after-treatment with some mordanting principle converts them into color lakes possessing excellent fastness to light, acids, washing and soaping.

Application of Mordant Acid Colors. It is only upon wool that the mordant acid colors are useful. They are dyed in the same manner as acid colors, but after the dyeing is completed the material is raised from the bath; from 1 to 3 per cent of potassium dichromate added and the boiling continued for from one to one and one-half hours. With some dyestuffs it is better to after-treat with the potassium dichromate in a separate bath.

Properties of the Mordant Acid Colors. The mordant acid colors when properly applied approach almost if not quite the fastness of the straight mordant colors. Difficulty is sometimes experienced in producing the exact shade desired, because the color produced at the end of the dyeing is often greatly changed during the after-treatment. It is not infrequent that a yellow or red will produce a dark blue, green or even black upon after-treatment.

As the after-treatment is almost without exception carried out with potassium dichromate, the mordant acid colors are often called "chrome colors."

Insoluble Azo Colors. A number of coloring matters of the azo type exist, the insolubility of which renders them non-applicable by any of the methods already described. Fortunately the nature of the process of their formation is such that they may be produced directly upon the fiber. Many insoluble azo colors may be produced, but only two, the so-called *para-nitraniline*, and *alpha-naphthylamine reds* have proved to be of practical value. These have been extensively used upon cotton during the past fifteen years, the former having replaced Turkey-red to a great extent.

The dyestuffs of this class are also known as *developed colors*, because they are developed during the process of application, also as *ice colors*, because ice is used to attain a low temperature during their formation.

The formation of the insoluble azo colors depends upon the fact that certain diazotized amino compounds produce insoluble coloring matters when brought into contact with certain naphthols or phenolic bodies. Para-nitraniline red, the most important example, is produced by padding cotton cloth with sodium beta-naphtholate, prepared by dissolving beta-naphthol in caustic soda solution, and then passing the cloth thus prepared through a bath containing a cold solution of diazotized para-nitraniline the latter being prepared by the action of nitrous acid upon para-nitraniline hydrochloride. As soon as the cloth prepared as above comes in contact with the para-nitraniline solution, a bright red develops which possesses excellent fastness to light and washing. If diazotized alpha-naphthylamine is substituted for the para-nitraniline a claret red color is produced of corresponding fastness.

The insoluble azo colors are not applicable to wool, owing to the fact that a strong caustic soda solution must be used in dissolving the naphthol which would act injuriously upon the fiber.

Reduction Vat Colors. The reduction vat colors have come into great prominence during recent years owing to their great resistance to practically all of the color destroying agencies particularly light and washing. The chemistry of their application is the same as that of indigo, in fact indigo is a reduction vat color in every sense of the word. As a class these colors are insoluble in water, but when strongly reduced in an alkaline bath they form soluble, usually colorless or almost colorless, reduction compounds which are easily absorbed by the fiber. Upon subsequent oxidation the reduced compounds pass back to the original or insoluble dyestuff which becomes fixed upon the fiber.

From the point of view of composition, the reduction vat colors may be divided into two classes, *first*, those directly *related to indigo*, *secondly*, those *related to anthracene*. The former may in most cases be applied to both cotton and wool but the latter only to cotton.

The coloring power of the reduction vat colors is weak and a comparatively large amount must be used in most cases.

Aniline Black. *Aniline black* is usually classified as one of the *miscellaneous colors* for it does not belong to any of the other groups. It is, in reality, an insoluble black pigment produced by the oxidation of aniline.

When aniline is oxidized three consecutive products are formed. (1) *Emeraldine*, a greenish colored salt insoluble in water. (2) *Nigraniline* formed by the oxidation of emeraldine, and (3) *Aniline black proper*, or ungreenable black as it is sometimes called, which is formed by a still further oxidation of nigraniline. The composition of the final product is not definitely known.

Aniline black is extensively used in calico-printing and the dyeing of hosiery but cannot be used successfully in wool dyeing.

In general aniline black is applied by preparing or printing the material with a mixture of aniline hydrochloride and certain oxidizing agents and oxygen carriers such as potassium chlorate, potassium ferrocyanide, copper sulphide, or vanadium salts, and subsequently drying and aging it by passing through an aging chamber.

Aniline black is extremely fast to light, bleaching and washing.

XXXIX

THE ART OF PAPER MAKING

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THE making of paper is one of the oldest of the arts. There has been found rolls of papyrus made, about 6000 years ago, by the ancient Egyptians out of the papyrus plant, a reed that grows to-day, wild, along the banks of the Nile. The Chinese, from whom the Europeans received their early instruction in the art, made paper from the inner bark of the mulberry tree upon which they made records of incidents that they desired to preserve for posterity.

Parchment made of the skins of animals was also used for many years for records. Erasures of old records were common, so that the parchment might be used again in order to save the cost of buying it anew. The chemist, in a number of instances has reproduced successfully these older records thus bringing to light some very valuable writings. Probably on account of the ease of making, using, carrying and handling these parchment rolls they came into general use.

Until about the year 1800, paper was made out of cotton and linen rags, using the crudest of machinery and producing what is called " hand made paper." Awakening along inventive lines in this art seems to have started somewhat before that time, as we have accounts published in 1765, suggesting the making of vegetable tissue into pulp and bleaching it into paper stock. Straw, wood, bark, hornets' nests, hopvines, cabbage-stumps, thistle stalks, burdock, and peat were all mentioned as suitable material for this purpose. To-day we have straw, peat, cotton stalks, bulrushes, bagasse manufactured into paper. The United States Government through an act of Congress, 1908, appropriated $30,000 for an experimental investigation of corn stalks as a basis for paper.

In about the year 1799, Robert took out a patent in France on a machine making endless paper. Not being successful there, he associated with him in London, Fourdrinier. They spent $300,000 which at that time meant more than it does now, in their endeavors to put into general use their machine. They were never rewarded, but their machine " The Fourdrinier " revolutionized paper making, a foundation upon which

has been built that which is to-day the ninth largest industry of the United States.

At the present time the manufacture of paper has two principal bases of supply. One of these is rags, the other is wood. Out of rags is made the highest priced paper.

Rag Paper. All linen and cotton rags can be converted into different grades of paper according to the kind and color of the rags. Great care is used in sorting rags before delivery to the paper mill so as to get a uniform kind of clean rags of same color. Buttons, pieces of metal, sticks, stones, and rubber, must be removed. Valuables such as money, jewelry—even diamonds, are often found in old rags.

The treatment of rags in the mill is as follows: The rags are delivered at the mill in strap iron bound bales about 3 ft. square and 5 ft. long. Often several hundred tons and sometimes two or three thousand tons are kept on hand, the quantity depends on chances to buy and the ready money of the mill owners.

The rags in bales as demanded for use, are taken to the ragroom where the bales are opened by women who make the final sorting, inspection and cutting. A scythe shaped knife is fastened in a vertical position to a table by which the operator cuts the rags, fine or coarse and also separates out the buckles, buttons, bones and other foreign matter that may be seen. The finest sort goes into the best of writing paper. From this high standard to the pasteboard and cheapest wrappers are many grades supplied by the different quality of rags. Mechanical cutters sometimes are used.

The rags next go to the *duster*. This machine dusts out often as much as 5 per cent of the weight of the rags. From the duster the rags are taken to the ragboiler. These boilers or rotaries are cylindrical shaped steel tanks 10 to 20 ft. long and to 6 to 8 ft. in diameter with heads riveted on each end, each having a journal for support as they rest in a horizontal position. A manhole for filling and emptying is placed midway. In this boiler the rags are cooked or boiled for several hours in a solution of caustic soda or a solution of milk of lime under a pressure of about 30 lbs. This cleans, destroys colors, and fits the stock for the beating engine, which is an oval shaped tub about 18 ft. long by 3 ft. high by 12 ft. wide at the center. This is a Holland invention for washing, beating and reducing the fiber of the paper stock. A partition extends as far as the rectangular part of the body. A shaft bearing a large roll that nearly fills one of the two partitions has heavy knives fitted into its face parallel to the shaft; these in revolving come as close as is desired to a fixed set of knives on the bottom floor. All the stock must pass between these two sets the moving one of which acts as a paddle wheel giving the motion to the stock around the *beater*. Fresh water is supplied so that the stock can be washed clean as well as reduced to the right length of fiber for the machine. In this beating engine the rags are, when desired, bleached for white

paper or are colored to whatever shade demanded. The stock is here sized when an engine-sized paper is to be made. This sizing is usually made of rosin and soda ash.

From the beater the stock is taken to a chest for storage in which it is stirred to keep it in liquid condition. From this chest the stock is pumped to a *Jordan engine* which is a cone-shaped plug about 4 ft. long that fits into a hollow cone made to receive it. In the surfaces of each are knives that can be made to come nearly together through which all of the paper stock must pass. From the Jordan the paper stock goes to the machine chest from whence it is pumped to the flow box where the right quantity of water is added to make it flow properly through the screens and onto the wire of the Fourdrinier paper machine that forms the sheet of paper.

The screens remove all particles too coarse to go into the sheet of paper as well as sticks or any foreign matter large enough to be held back from passing through the slots which are twelve-hundredths of an inch in width. The wire is one of the most important and costly parts of the machine costing $100 to $200. Upon it the paper is formed or made. This wire is made endless, with ends woven together so that it will pass around the rolls as an endless belt, supported by a series of brass rolls placed at various positions as demanded by the work to be done. The wire is stretched out like a horizontal oblong table the width of which determines the width of the sheet of paper. The mixture of stock and water is flowed onto the wire as evenly as possible. It must be perfectly done too as, if it is imperfect, it cannot be sold and is put back into the beaters to be beaten up and worked over again. The sheet of paper is formed at this place at the rate of 60 or 80 ft. a minute as in fine writing-paper, or 600 or more feet per minute as is done on the news print machines.

At intervals before the wire reaches the first press, suction boxes are placed to suck out some of the water. There is also often a dandy roll that places a name or figure in the paper, such as one can see when it is held up to the light. This stamps the name into the sheet of paper while it is wet and is sometimes called a "water mark." The paper is fully formed on the wire although saturated with water that must be gotten rid of. The sheet is made to pass between two heavy press rolls that squeeze out a quantity of water then through a second press and sometimes through a third press the aim being to extract as much water as can be gotten rid of mechanically by presses and suction boxes. Two-thirds of the weight of the sheet of paper before going to the steam dryers is water. The dryers are hollow cast iron cylinders 3 or 4 ft. or more in diameter and 80 or 90 ins. up to 180 ins. long as the width of the sheet of paper may require. The end of the sheet of paper is carried by hand to the first dryer which as all the others is steam heated. The dryers are in two or three rows one on top of the other for economy of space. Around these passes the sheet of paper, making contact with as much of the hot face

FIG. 327.—Fourdrinier.

of the dryer as is possible. As it passes under a dryer it would naturally fall out of contact. To prevent this a heavy cotton duck felt is run so as to hold it up against the dryer. The *dryers* may be from 16 to 50 in number according to the character of the paper made. The paper contains 6 to 10 per cent of moisture when it leaves the dryers. Thus you will see for every ton of paper dried two tons of water are evaporated and this must be done by steam. From this point it is generally passed by hand through a stack of calenders that smooth out or polish the surface of the sheet. From the *calenders* (Fig. 328) it passes to the reels and from the reels through the slitters that cut the sheet into the width desired and to the *winders* where it is wound up into large rolls. When demanded these rolls are taken to an apparatus called a super-calender where the surface of the sheet is further polished by running through heavy steel rolls and then

Fig. 328.—Calenders.

it goes to the *cutters* where it is cut up into any size of sheets demanded. From the cutters it goes to the counters. These who are generally girls count out the sheets into 12, 24 or 500 sheets ready for the finisher and packers who make up the packages of paper as are ordered for the trade.

Wood Paper. As late as 1875 our common daily newspapers were made from rag stock and one single sheet or a four-page newspaper at that time cost from 2 to 5 cents per copy, and old papers were worth one cent each. The newspapers of to-day are made from wood and we have papers with many pages sold for one cent per copy. Ordinary newspaper in 1876 sold for \$164 per ton. To-day newspaper is selling at about \$40 per ton. All this has come about through the development of the manufacture of paper from wood.

The supplying of the mills with wood is a great industry in itself. In the fall of the year men are sent into the woods in crews of ten to one hundred and sometimes more with horses, wagons, sleds, and feed. There they fell the trees, trim them of branches, cut the trees into timber or cord wood lengths and get ready either to float the lumber down the stream in a " drive " or to haul it to some nearby railroad so that it can be delivered to the mill where it is converted into paper.

On the arrival of the wood at the mill, if it is to be chemically treated, it is generally piled up so that it may dry, it is allowed to thus season in the pile for one, two or perhaps three years. This seasoned wood loses

much of its sap and water and requires less chemicals to convert it than the green wood directly from the forest. For the mechanical pulp a fresh green wood produces better fiber and is easier ground up than the dry seasoned wood. For any of the treatments the bark must be removed, which is done by a machine called a *barker* or by the hand draw shave.

In the wood paper industry the principal methods of treating wood to produce fiber are by grinding, producing ground wood or mechanical fiber and cooking by either the caustic soda or the sulphite process.

The transformation of wood into paper is an interesting chemical and mechanical process. Out of the spruce, hemlock, fir and poplar we obtain practically all of our newspaper, nearly all even of our book paper, and a large portion of our writing papers.

Mechanical Process. The mechanical process consists of placing blocks of wood about 18 ins. long in apertures called pockets of a heavy cast-iron frame that encases a large grindstone. This grindstone revolves at about 200 revolutions per minute, a stream of water plays against its face to keep the wood from burning, as it is pressed against the face by hydraulic pressure of about 30 lbs. The result of this is the reduction of the wood to a fine pulpy mass which is called mechanical pulp or ground wood. This is floated by water on to a coarse screen by which the pieces of wood that have not been ground up are removed. The pulp goes to a fine screen through which the mechanical pulp that is of the right kind to go into the making of a newspaper or other papers passes. This pulp now goes to the beater room to be mixed with sulphite pulp or other stock according to the grade of paper it is desired to manufacture, or to a wet machine, which is an apparatus for getting the pulp into a state dry enough to handle. The wet machine is a wooden vat 6 ft. wide 8 ft. long and 5 ft. deep into which the mixture of water and ground wood is pumped. A bronze cylinder about 3 ft. in diameter by 6 ft long covered with a brass wire net of 60-mesh is immersed in the mixture in such a manner that the water passes through the meshes of the wire leaving the pulp sticking to it. A coarse woolen blanket called a felt is pressed against the cylinder mold by a heavy couch roll. The blanket automatically picks off the pulp from the cylinder, carries it along on its surface over a suction box and through heavy press rolls that extract quantities of water from it and leaves it with from 35 to 50 per cent of pulp. One of the rolls of the press is of hard maple wood which picks the pulp from the blanket when it comes in contact with it. As the press roll revolves the pulp is continuously added to it from the blanket until the sheet is thick enough in the judgment of the Press Tender who then with a sharp pointed wooden pin cuts it off by passing the point under the sheet close to the wood roll. The sheet of pulp is rolled off on a table folded up, weighed and is then ready for shipment or storage.

Chemical Pulp is made by treatment with either caustic soda or bisulphite liquors. Soda fiber is made by treating poplar and similar

wood with caustic soda in digesters, which are large steel boilers. This process was put into practical use in 1875, sulphite fiber, perfected in 1885 is made by treating spruce and similar woods with sulphurous acid, combined with lime and magnesia, in special digesters made to withstand the action of the corrosive acids.

Soda Process. The caustic soda liquors are made in the paper mills using this method by dissolving soda ash in water and to this solution adding about 55 to 60 per cent of freshly burnt pure quick lime bringing the mass to a boil, mixing it thoroughly by stirring, then allowing the calcium carbonate, which is produced by the reaction with the soda ash, to settle to the bottom. The clear caustic liquor is siphoned off, the lime sludge is washed two or three times with water to remove as much of the caustic soda as possible. Attempts have been made to reclaim this lime sludge by drying it and reburning it, but this is seldom done.

Poplar Wood and its kindred species are principally used in the soda process as they yield easiest to this treatment, requiring a smaller amount of caustic soda for reduction than do other woods. The well-seasoned wood from the piles, where it has lain for a year or more, is brought to the mill where it is inspected and all dirt and black knots removed, as these make objectionable color in the pulp and paper. These sticks of wood are then taken to a machine called a *chipper* which slices off the wood into chips about $\frac{7}{8}$ in. long in a similar manner to slicing an onion. The thickness of these chips will generally be the annual growth of the wood. The chips are screened to remove the sawdust, knots and coarse pieces. These coarse pieces passing through a re-chipper are reduced to the proper sizes. As the sawdust produces a fiber which is too short for use and if allowed to remain mixed with the wood would consume a proportionate amount of chemicals it is carefully screened out and is used for fuel. Many experiments have been tried for the utilization of sawdust for fiber but none have proved successful. The chips are stored in large bins placed over the digesters into which they are run through spouts by gravity. These *digesters* for the soda process are made of steel 1 inch thick and are sometimes 50 ft. high and 10 ft. in diameter. They are filled full of chips and then is added a certain amount of the caustic soda solution of a density of 8 to 10° Bé. according to the character of the wood to be cooked. When filled, the cover of the digester is bolted down and steam is turned on through the bottom. In the soda digesters there is a false bottom which allows the hot liquor to pass down through it. There is generally an ejector under this false bottom through which ejector steam is passed which lifts the cooking liquor at the bottom, carries it through a pipe to the top of the digester and sprinkles it over the chips, thus making a continuous circulation which produces thorough cooking. The cooking of the chips dissolves the woody matter. When completely cooked, the contents of the digester will be found to have shrunk one quarter to a third of its bulk, but the chips retain their original form at this point.

A cooking pressure of 90 lbs. is maintained in the digesters for from eight to ten hours when a sample is drawn to ascertain if the wood is properly cooked. When the operation is completed a valve of 6 or 8 ins. diameter at the lower part of the digesters is opened and the entire mass is violently blown out of the digester by pressure into a suitable receiving tank. This violent action and the impact of its contents serves to shatter or destroy the original form of the chips and a pulpy mass of fiber results. The liquor which has been employed for the reduction is carefully drawn off, evaporated to a consistency of 35 to 40° Bé. by means of some suitable evaporator. It goes now to a rotary furnace where it is further dried and the tar and other wood products are burned up leaving the soda mixed with charcoal. This black mass is called "black ash." The soda which it contains is leeched out and is used over again with addition of fresh soda ash and caustic lime. A recovery of from 85 per cent to 90 per cent of the original soda ash used is generally obtained, and this materially reduces the cost of chemicals employed. The profits of the mill are largely dependent upon this part of the manufacture. All soda fibers when cooked and washed clean from the cooking liquors are somewhat colored, and if a white paper is desired they must be bleached to the desired whiteness. If a colored paper is demanded, the color desired can be made in many cases without recourse to bleaching. The pulp when washed clean is passed through screens which remove from it uncooked wood and coarse matters and either goes to the beaters where it is mixed with other fibers to make the desired grade of paper or it is bleached if required and then pumped to the wet machines previously described, to put into condition for handling in shipment or storage. Soda fiber is a soft stock and is largely used in the better magazine, book and writing paper grades. It is of a soft, spongy-like feeling to the fingers and is a quality desired in paper used for books. It is a fiber that does not deteriorate by time as the chemicals that have produced it do not have a rotting effect upon it unless it is overbleached. Its selling price when bleached is about $45 per ton.

Sulphite Process. The largest amount of chemical fiber is produced by this process. The spruce, fir and hemlock from which most of this pulp is made is piled, dried, cleaned, chipped and screened and conveyed into the chip bins above the digesters practically in the same manner as for the soda process. The digesters for this process are built of heavy 1 in. thick steel and are very large, being often 50 ft. high by 18 ft. in diameter made to contain 20 to 30 cords of wood at a charge. On the inside of these digesters there is generally placed a protective lining of cement, or composition and a brick lining because the acid, if it comes in contact with the steel would attack it. Great care is used in protecting the inside shell and in properly conducted mills examinations are made of it after each blow to see that no injury is taking place.

These digesters are loaded full to the top with chips and bisulphite liquors

run into the digester to within about 3 ft. of the top. This bisulphite acid or cooking acid is made by burning sulphur in specially built furnaces. In some of the countries of Europe pyrites, on account of its cheapness, is used instead of the sulphur, but it has not been found profitable to use pyrites in this country. The greater part of the sulphur used in this country to-day comes from the underground sulphur mines of Louisiana. This is obtained by forcing super-heated steam down a pipe which melts the sulphur and it is forced up in the casing as a brown liquid and is run off into piles where, when it is cooled it returns to its yellow sulphur color. This Louisiana sulphur has practically driven out of the market in this country the Sicilian sulphur which was first used. When the Louisiana sulphur came into use much trouble was caused by the impurities that it contained which would form a coating over the molten surface and prevent the formation of the sulphur dioxide gas. This difficulty is now overcome by the invention of rotary and agitating burners. This gas is generated by burning sulphur in the furnace admitting the right amount of air so that the chemical combination of two atoms of oxygen with one of sulphur may take place. To further insure this a combustion chamber is attached back of the furnace where a further supply of air is carefully admitted bringing the sulphur dioxide gas to 14 to 18 per cent. This gas first goes through cast iron pipes to cool it, then it enters lead pipes immersed in cold water to further reduce the temperature. It next passes successively through three or four wooden tanks containing a mixture of milk of lime that absorbs the gas as it comes in contact with it. The lime best suited for this purpose is made from dolomite often carrying 45 per cent of magnesia. The gas enters the tank at the bottom leaving at the top, mixing with the milk of lime in successive tanks till the sulphur dioxide is finally all absorbed and the residual air passes out of the heavy vacuum pumps that " pull the gas from the furnace to them."

The gas may be absorbed by the tower system, when it is passed into towers about 100 ft. high where it comes in contact with limestone and water and by its acid action on the lime rock produces the liquor necessary for the reduction or cooking of the wood. The strength of this acid is tested by iodine solution using starch as indicator and is generally run at a Beaumé strength of 4 to 6° containing the proper amounts of free acid and combined acid according to the wood that is to be cooked.

The digester having its complement of acid is sealed and relief pipes are connected to the top cover. This digester has no false bottom and the steam is applied directly at its cone-shaped base. The circulation of this digester depends on the passage of the steam into the bottom working its way up through the mass of chips and liquor causing the sulphur dioxide to break loose from its combination with the lime and magnesia and the resultant gas is relieved through the escape valves and pipes on the top of the cover. This gas as well as the liquor that is blown out through the relief pipes is valuable up to two-thirds or more of the time of the cooking.

They are cooled by running them through lead pipes immersed in cold water and are mixed with fresh cooking liquors. This is the only method of reclaiming the sulphur in use at present. There has not thus far been invented any system of circulation for the sulphite cooking such as is in use in the vertical soda digesters. Both the soda and sulphite processes have digesters or cookers that are placed horizontally and are rotated but they are not used as much as the vertical or upright digester on account of the extra labor required to fill and to dump them. The vertical digesters are self emptying thus lessening the cost of labor and time.

In the cooking of the sulphite pulp in the digester the mass of chips shrinks as it does in the soda process. During this process a pressure of 90 lbs. is maintained in the digester and the temperatures run as high as 350°. The quick cooks are made in six to ten hours, the slow cooks are steamed from thirty-six to seventy-two hours. The slow cook produces the strongest fibers that we have and it uses a weaker strength of chemicals than the quick cooks. The vertical digesters are discharged in a similar manner as with the soda ones. The pulp on being blown out strikes a bronze plate called a *target* and is almost white. The cooking liquor is at once washed out of the pulp by flooding the tank into which it is blown with fresh clean water. The tank has a perforated bottom connected to the sewer with a valve so as to control it easily. The water used for this washing strange to say, must be pure and more care taken to insure its cleanliness than with the water we generally drink. This waste liquor has been experimented on extensively but up to the present time it is found to be of value only in tanning and as a binder for slack coal in making bricquets for fuel. The cooking acid must be thoroughly washed out of the sulphite pulp because if it is not the color of the pulp will turn pink or darken to a light gray slate color. After washing, the stock is passed through screens with mesh not finer than $\frac{1}{16}$ in. through which the fiber itself passes leaving behind the knots and uncooked pieces and coarse stuff, which are sent to the scrap heap to be ground up. When sulphite pulp is to be shipped to another mill or piled up and stored it is run over the *wet machine* which has been previously described. If there is a newspaper mill connected with these plants, the ground wood and the sulphite are each pumped to it and mixed together in beater engines. For the common newspapers of to-day 75 per cent of ground wood pulp is mixed with about 25 per cent of sulphite pulp, some alum is added and a little pink and blue aniline to give it the required white tint. After beating in the engine from a quarter to a half hour, the stock is dropped into a stock chest from whence it is pumped to a Jordan engine, which shortens the fiber to the proper length for the sheet of paper. From the Jordan engine it goes to the stock chest that supplies the paper machine being the same type as the one used to make rag and writing paper upon only it is much heavier, costlier and runs faster. Some of these machines cost as much as $80,000 each

and are marvels of beautifully adjusted mechanism. The different parts are so accurately adjusted that from the flow of the wet stock onto the wire to the winding up of the dried sheet of paper as it comes through the calenders it moves with perfect adjustment whether the speed be 300 or 650 ft. per minute.

At the beginning of the use of wood for paper stock few if any of the mills owned any timber lands, now all endeavor to buy all growing timber they are able to obtain. In 1882 wood of good size, 8 ins. to 18 ins. and more in diameter cost $2.50 to $3 per cord at the mill. Wood prices to-day run from $6 to $16 generally being $10 or $12 per cord of 128 cu.ft. As regards the size often one-half of the wood now obtained will not be over 3 ins. in diameter a size that in the earlier days would have been sent to the fire-room. The owners of timber lands are now cutting their holdings more carefully, often under the personal directions of U. S. Forestry Officers thereby testifying that the conservation of the forests is no idle talk.

The production of print paper is now estimated at 8,000,000 tons annually. Of this 75 per cent is ground wood stock 25 per cent is sulphite stocks. As one and one-half cords of wood are required to make a ton of newspaper, 12,000,000 cords per year or 40,000 cords daily are used. Allowing 10 cords of wood per acre which is high, in all but the Pacific Coast region where 80 to 200 cords are not uncommon, this means that 4000 acres of land are daily stripped of wood to furnish paper. The United States produces 40 per cent of the paper and accordingly it uses up 1600 acres of woodland every day. There has been an advance in the cost of labor. In 1882 all pulp and paper tour work was done in eleven- or thirteen-hour shifts now in many mills there are three daily shifts of eight hours each. Common labor that was $1.25 per shift has gone to $1.67 or $2, while the machine tenders price has advanced from $2.50 to $4 and the other grades of labor are increased correspondingly. The production of all mills has been increased. Grinders are now made that produce five tons of ground wood as against one and a half or two tons before made. Digesters now produce ten to fifteen tons of pulp against, three, four or five tons ormerly with the same crew to handle them and the same time to cook the stock, also one of the big newspaper machines of to-day will make three times as much paper as a machine in 1882 could make using the same four men to run it.

The force of some of the other departments must be largely increased to keep pace with the work. Machinery is used whenever it can be employed advantageously so as to cut out manual labor. Whenever possible this class of mills is located where a water-power of at least 2000 horse-power can be utilized also the large quantities of water used must be pure and clean. Much care is taken in purifying the water for use in the mill, settling tanks, alum coagulators, filters, etc.

The wastes of the wood are used for fuel. Other wastes such as

worn-out, broken machinery, pulleys, belts, different castings of brass, lead, iron and bronze, also wires and woolen felts bring some return but the waste of chemicals and fiber, that in many mills reaches as high as 10 per cent is the most costly. This is run into the river and all lost. Some of our mills make 100 to 250 tons of paper daily or 30,000 to 75,000 tons annually. In the mill producing 100 tons per day the waste per year at this rate would be at least 3000 tons which at $50 per ton would amount to $150,000. The larger plant making 250 tons of news print to-day would lose more than 8000 tons of stock which would bring at $50 per ton or $400,000. Some attention is being paid to this most costly loss, but not enough has been accomplished to prevent a large waste even to-day.

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EXPLOSIVES

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An explosive is a substance, or mixture of substances, which by proper means may be caused to decompose with great violence in such a way as to produce useful results, such as the shattering of rock or the propulsion of projectiles. A great many substances which may be classed as explosives are now known to chemistry, but for practical purposes only those explosives which can be cheaply manufactured on a large scale are of commercial importance.

There are many ways in which explosives are used. No one explosive has been found which will answer all purposes. Dynamite cannot be used as a propelling agent in firearms, and smokeless powder is not employed as a substitute for dynamite in ordinary blasting. Explosives suitable for military purposes must conform to requirements quite different from those demanded for technical purposes; and an explosive suitable for use in a stone quarry might be totally unsuited for use in a coal mine. In consequence of these varying requirements the explosive industry is rather highly specialized.

The number of different explosives which have been patented and manufactured is large. The most important commercial classes are:

1. Black powder and similar mixtures.
2. Explosives consisting of nitrocellulose or nitro-starch.
3. Explosives consisting in whole or in part of nitroglycerin, dinitroglycerin, diglycerol nitrate, and other derivatives of glycerin.
4. Various aromatic nitro compounds, such as picric acid.
5. Fulminants or detonators, of which mercury fulminate may be regarded as a type.

Vast improvements in the manufacture and use of explosives have been effected within the past twenty years, and, considering the progress now beng made, it is very likely that the next twenty years will witness further deivelopments.

Black Powder. Black powder, or ordinary gunpowder, was the only explosive in general use up to about fifty years ago. It is said to have been discovered in the thirteenth century, but its origin as well as the

identity of its inventor is involved in an obscurity which probably can never be cleared. The first powder mill is said to have been erected at Augsburg in 1340, and from that time to this black powder has retained, with very slight variations, the composition given to it by the first powder makers. Although inferior in strength to many explosives recently discovered it is still being manufactured on an enormous scale.

For a long time after its discovery black powder was used exclusively for military purposes. Its peaceful application to the mining industry began about two hundred years ago.

Composition. Typical black powder is an intimate mixture of potassium nitrate, wood charcoal, and sulphur. It is generally manufactured in granular form, the individual granules having a slight coating of graphite. The composition of black powder varies slightly in different countries. Guttmann gives the following table for the powders most commonly used.

	Saltpeter.	Sulphur.	Charcoal.
	%	%	%
Germany	74	10	16
France	75	10	15
England	75	10	15
Holland	70	14	16
Italy	75	10	15
Austria	75	10	15
Russia	75	10	15
Switzerland	75	11	14
United States	75	10	15

The process of manufacture consists simply of mixing thoroughly the constituents, and of forming the mass into grains of different sizes as required for different purposes.

The Raw Materials of Black Powder. The potassium nitrate (saltpeter) used in manufacturing black powder is either "natural" saltpeter or the so-called "conversion" saltpeter. "Natural" saltpeter is obtained by subjecting nitrogenous organic matter to decay in the presence of wood ashes. It has been manufactured in this manner from early times on a large scale in India. "Conversion" saltpeter is obtained by treating a solution of potassium chloride (Stassfurt salts) with the solution of a soluble nitrate, such as sodium nitrate from the Chili nitrate fields.

Natural saltpeter is preferred for powder making, since the conversion saltpeter frequently contains traces of potassium or sodium perchlorates, the presence of which makes the powder less uniform and less reliable. The better grades of sporting and military black powders are made from the natural saltpeter.

Charcoal which has been made by charring peeled, well-seasoned willow wood is preferred for powder making, although many other kinds of wood, and even hemp, flax and straw are used. For certain kinds of

powder it is required that as much as possible of the volatile matter be driven off. For other kinds the wood is only partly carbonized, when the charcoal instead of being black has a red or brown appearance. These brown coals are used for making sporting powders and were formerly used exclusively in military powders for large calibre guns.

The sulphur used in black powder manufacture is ordinary sulphur, as free as possible from impurities.

Process of Manufacture. The technical process of mixing these ingredients involves a number of separate operations as follows:

1. Pulverizing the raw materials;
2. Mixing the raw materials;
3. Compressing;
4. Graining;
5. Drying;
6. Dusting and sorting;
7. Polishing;
8. Blending.

The raw materials are first pulverized in revolving drums containing bronze balls. For this operation they are taken in pairs; that is, saltpeter and sulphur; saltpeter and charcoal; charcoal and sulphur. The different pairs are then mixed in proper proportion and further ground in the ball-mill. In this condition the powder is known as " meal " and may be used without further treatment for making fireworks or fuses. It is not, however, in a form suitable for blasting or for use in firearms.

The grinding in the ball-mill serves merely as a preliminary mixing. To secure a more thorough incorporation of the raw materials, the meal is next ground in a mill provided with heavy edge runners. This is a type of mill extensively used in many industries (Fig. 6), and consists of two heavy, broad-edged wheels, connected by a short axle which is caused to revolve horizontally by an upright shaft. The two wheels or runners travel around a circular basin which contains the material to be ground, and which is subjected to a combined crushing and grinding action. This operation lasts about four hours. Before grinding under the edge-runners, about 10 per cent of water is added to the powder to reduce the danger of explosion by friction. In spite of all precautions the mass frequently explodes and for this reason no person is allowed in the grinding room while the runners are in motion, the mills being started and stopped from a distance.

After the grinding is complete the mass is pressed into sheets, and the sheets subjected to further pressure and consolidation in a hydraulic press. The pressure employed in these hydraulic presses varies from 100 to 110 atmospheres, the powder remaining in the press for from one-half to two hours. Sporting powders are pressed so as to obtain a specific gravity of 1.7 or 1.8, while the specific gravity of blasting powders is only about 1.5.

The cakes are next broken up and the fragments passed through sieves of different mesh, which sort the material into grains of uniform

sizes, the grains ranging from 0.3 millimeter to 1.8 millimeters in longest dimension. The next step is to remove the greater part of the added water by means of dry air at a moderate temperature. When the moisture has been reduced so that the powder contains from 1.5 to 3 per cent. depending on the grade, it is again sifted so as to remove dust, which is returned to the grinding mill. The powder is then polished by rotating in wooden drums. This serves to rub off sharp corners. After a further sifting to remove dust, the powder is polished by shaking in the drum with a small quantity of graphite. Different grades of powder may be blended, as required, after which the finished product is packed for the market in air-tight packages.

Chemistry of Black Powder Explosions. The action of black powder as an explosive depends on the fact that on ignition the carbon and sulphur are rapidly burned at the expense of the oxygen of the potassium nitrate, whereby large volumes of gas are liberated. The temperature of combustion being very high the gas tends to increase enormously in volume; and if the space in which the combustion takes place is limited, it exerts an enormous pressure and hence is able to rend obstructions, or propel shot. The ideal reaction of decomposition of black powder is:

$$3KNO_3+3C+S=K_2S+N_2+3CO_2.$$

But the products of decomposition vary greatly under different conditions. In general, black powder in decomposing gives off about 43 per cent of its weight of gaseous products and 57 per cent of solid products. Thus more than one-half of the products of decomposition contribute nothing directly to the force of explosion. This is one of the reasons why black powder is one of the least effective explosives in general use.

Explosives Similar to Black Powder. A large number of mixtures similar to black powder have recently been introduced. Sodium nitrate is sometimes used in blasting powders instead of potassium nitrate as the oxygen carrier. Such powders, however, are of limited applicability on account of the readiness with which sodium nitrate absorbs moisture.

Powders containing potassium chlorate as oxygen carrier are much more powerful than powders containing nitrates, but on account of the sensitiveness of these chlorate mixtures they are uncertain in their action and dangerous to handle. The manufacture or sale of such powders is forbidden in most countries.

A very powerful explosive known as "ammonal" is extensively used in Europe. This consists of a mixture of finely pulverized metallic aluminium and ammonium nitrate, which ideally decomposes according to the equation:

$$2Al+NH_4NO_3=Al_2O_3+2N_2+3H_2O+H_2.$$

Unlike black powder, ammonal cannot be set off by simple ignition, but must be exploded by a shock from the explosion of a priming charge of some fulminant, such as mercury fulminate.

Nitrocellulose. Nitrocellulose, or more properly speaking, cellulose nitrate, is now the chief material used in the manufacture of military and sporting powders throughout the world. In conjunction with camphor and other substances it is also largely used in making celluloid.

Nitrocellulose, is not a nitro-compound, as chemists now understand that term, but is a true nitrate in which the hydroxyl groups of the cellulose molecules have been replaced by the nitrate radicle (NO_3). The inaccurate designation, nitrocellulose, which was given to the substance by its early investigators has however been so long in use that it is not likely to be supplanted by the more correct term. Nitrocellulose is manufactured by subjecting cellulose to the action of strong nitric acid under certain definite conditions.

Raw Materials of Nitrocellulose Manufacture. The raw materials used in making nitrocellulose are cellulose (in the form of wood pulp, tissue paper, cotton wool, or cotton wastes from spinning mills) and sulphuric and nitric acids. For making nitrocellulose to be used in the cheaper grades of celulloid and in certain cheap commercial explosives, wood pulp or paper may be used. For making smokeless powders for military use, only the best and purest forms of cellulose can be employed, such as cleaned and bleached cotton wool and spinning mill wastes. The so-called delint cotton is mostly employed.

Preliminary Treatment of the Cellulose. The cotton wool or wastes must first be deprived of all impurities such as oil, fat, or dirt. This is done by boiling with dilute alkali. This treatment is next followed by light bleaching by means of calcium hypochlorite, for the purpose of removing lignin substances that form unstable nitrates which would impair the stability of the product. Too vigorous a bleaching is to be avoided, as otherwise hydrocelluloses or oxy-celluloses would result and give rise to unstable nitrates.

Before the bleached cotton is subjected to the nitration it is dried so as to reduce its moisture content below 1 per cent. For this result exposure to a temperature of 105° C. for several hours is usually necessary.

The Process of Nitration. Nitrocellulose is not a definite compound of invariable composition like calcium nitrate. The cellulose molecule can be made to take up about 14 per cent of nitrogen, but below this maximum products of many degrees of nitration can be obtained. Products of similar nitrogen content prepared under closely similar conditions may differ widely in properties. For this reason practical operations have to be carried on with great attention to detail.

The process of manufacture in outline consists in dipping the cotton into a mixture of strong nitric and sulphuric acids, allowing to stand for a short time, and then removing the acid and purifying the nitrocellulose.

The degree of nitration and the properties of the product are dependent on the temperature of nitration, duration of the action of the acids, ratio of the mass of cotton to the mass of acids, and relative proportions of sulphuric acid, nitric acid, and water in the acid mixture. A variation in any one of these factors affects the degree of nitration.

Nitrocellulose for use in military smokeless powders is made by nitrating cotton at 30° C. with a mixed acid containing 63 parts sulphuric acid, 22 parts nitric acid and 53 parts of water. A nitrocellulose thus made will have a nitrogen content of from 12.50 to 12.70 per cent and will be completely soluble in a mixture of 2 parts of ether and 1 part of alcohol. Nitrocellulose of over 12.75 per cent is generally insoluble in the ether-alcohol mixture. Nitrocellulose containing 13.10 to 13.40 per cent of nitrogen is chiefly used for small arm powders and submarine mines. Nitrocellulose for use in celluloid manufacture and for making artificial silk contains from 8 to 11 per cent of nitrogen.

There are several forms of apparatus used in the operation of nitrating. The most general practice is to conduct the operation in a lead-lined iron pot or centrifuge. The mixed acid of the desired strength, which has been warmed to the required temperature, is run in through a pipe leading from the acid reservoir, and the requisite amount of cotton is submerged in the acid. The bowl of the centrifuge is then covered and allowed to stand undisturbed for the requisite length of time. The fumes given off during the reaction are led away through a wide pipe. At the end of the nitration, the centrifuge is set in motion and the excess of acid removed from the nitrated product by centrifugal force. The nitrocellulose is taken out of the bowl with pitchforks, thrown into large tanks filled with water, whereupon the centrifuge is ready for a new charge.

The reaction whereby nitrocellulose is formed from cellulose and nitric acid is as follows:

$$C_{24}H_{40}O_{20}+nHNO_3=C_{24}H_{40}-nO_{20}(NO_2)_n.$$

In this equation n represents any number between 1 and 11.

The sulphuric acid, which constitutes more than three-fifths of the acid mixture, takes no direct part in this reaction, its function being to absorb the water resulting from the chemical process, thereby keeping the nitric acid up to its full strength. This is the usual explanation of the reason for using sulphuric acid, although it may not be the true one.

Purifying the Nitrocellulose. The nitrocellulose requires thorough purification in order to prevent it from undergoing spontaneous decomposition at some later period of use or storage. To effect this purification it is repeatedly washed and boiled with clean water; but a simple boiling, even if prolonged, is not sufficient. The cotton fibre is hollow, and in this hollow space traces of acid and by-products may remain to cause trouble later on. To insure the complete removal of these impurities the crude nitrocellulose, after a preliminary boiling, is finely pulped in a

" beater," very much like the " beaters " used in paper mills, after which it is repeatedly boiled and washed in fresh water.

The attainment of a satisfactory degree of purification is recognized by heating a sample of the product, contained in a test tube in which is suspended a strip of filter paper which has been dipped in a solution of potassium iodide and starch to 65° C. If no iodine is liberated within sixty minutes, the nitrocellulose is regarded as stable; otherwise the washing and boiling must be continued. The whole process of boiling, washing, and pulping usually requires several days.

When finally purity has been obtained the nitrocellulose is usually worked immediately into the finished products. Where such working up cannot be at once proceeded with it is kept under water, or in a very moist state, to obviate the danger of explosion. If it has to be dried, this operation must be conducted with care for the same reason. Nitrocellulose is seldom stored or transported unless it contains at least 15 per cent of water. In outward appearance nitrocellulose does not differ from the cotton from which it is made, except that is has a somewhat harsher feel.

The Displacement Process of Nitration. A more recent process of nitrating, one which in many respects is more advantageous than nitrating in centrifuges, is the displacement process. Fig. 329 is a schematic diagram showing in principle the construction of an apparatus of this type. The circular stoneware vessel A, having a conical depression at the bottom from which leads the pipe B, is provided with a perforated stone false bottom F, on which the cotton to be nitrated is placed. By a suitable arrangement of pipes, mixed acid is admitted into the vessel until the cotton is covered with it. The cotton is kept submerged beneath the acid by the weight of the movable cover D, which is also perforated.

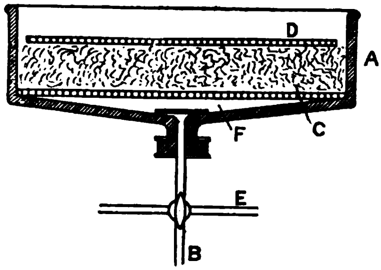

FIG. 329.—Nitrating vessel used in displacement process of making guncotton.

Over the opening of B there is a fine sieve to catch particles which pass through the perforated bottom of the vessel. After the apparatus has been filled with cotton and acid and the movable cover is in position, a small quantity of water is poured over the surface for the purpose preventing the escape of fumes. This water comes in contact with the acid only at the edges and in the perforations of D. Under these circumstances the acid and water remain in sharply separated layers. The vessel and its contents are now left to themselves for about an hour, when the stop-cock is opened and the acid allowed to flow off slowly by gravity, water being led in at the top as fast as the acid flows away at the bottom, until the acid has been completely displaced from the appa-

ratus. No mixing of acid and water, and no noteworthy rise in temperature occurs during the displacement. After a preliminary washing in the same vessel, the nitrated cotton is removed and purified as usual. The displacement process of nitration requires more time than the centrifugal process, but it has distinctive advantages in the absence of fumes, less labor required, and greatly diminished expense for repairs.

Regeneration of the Acids. During the nitration the acid mixture falls in strength owing to the loss of NO_3 and increase in water content, both being due to the chemical reaction. After being drawn off from the nitrating vessel, the spent acid must be " fortified " by addition of strong acid before it can be used again for nitrating.

Smokeless Powders. Powders made from nitrocellulose and other pure organic nitro-compounds are called smokeless powders on account of their comparative freedom from ash. Black powder, as has been said before, when burned leaves behind over one-half its weight of solid products, which naturally give rise to dense clouds of smoke. As the mineral matter of nitrocellulose rarely exceeds 0.5 per cent the residue left on combustion of powders made from it gives rise to very little smoke.

Owing to its extreme rapidity of combustion, pure nitrocellulose cannot be used in firearms, but must be made into a form wherein the rate of combustion is greatly reduced, otherwise the gun or cannon might be shattered. This transformation is effected by working the nitrocellulose into a stiff dough with a small amount of ether-alcohol mixture. The plastic mass thus formed is then run through a press similar to a macaroni press, which forms it into long rods having one or more axial perforations. In most cases there are seven of these perforations. These rods are then cut into suitable lengths, each length constituting a " grain " of the powder. The heavier the gun in which the powder is to be used, the larger are these " grains." For example, a " grain " of powder for a 12-in. gun is about 3 ins. long with a diameter of about $\frac{3}{4}$ in. Not all military powders have the same form, however, as the ordnance experts of the different countries have different preferences in the matter.

The final step in making smokeless powder is to reduce the content of volatile matter, water, alcohol and ether by drying to within certain very definite limits.

Instead of working the nitrocellulose into a colloidal mass with ether-alcohol, acetone may be used either alone or in conjunction with nitroglycerin, or other nitro-compounds. Nitrocellulose powders with a nitroglycerin base are more uniform and reliable than straight nitrocellulose powders, but are more corrosive to the interior surface of the gun.

Nitro-starch. Nitro-starch or rather starch nitrate, has lately been successfully manufactured for use as a blasting explosive, in smokeless powders, and in general for all purposes to which nitrated cotton is put. Cassava starch is the most suitable variety for this purpose. The process of manufacture differs somewhat from the manufacture of nitrocellulose,

the points of difference being in the use of stronger acids, and appropriate means for mixing the starch with the acid and separating the product therefrom. The advantage of starch over cotton is its comparative cheapness. The nitro-starch is more difficult to stabilize than the nitro-cotton. The methods used in making it are as yet trade secrets.

Nitroglycerin and Dynamite. Explosives composed wholly or in part of nitroglycerin and closely related substances are at the present time the most important of industrial explosives.

Nitroglycerin is formed from nitric acid and glycerin in accordance with the following reaction:

$$C_3H_5(OH)_3+3HNO_3=C_3H_5(NO_3)_3+3H_2O.$$

Nitroglycerin, like the analogous product of the interaction of nitric acid and cellulose, is a true nitrate and not a nitro-compound. The term "nitroglycerin" is therefore a misnomer, which, however, is apparently too well intrenched in common usage to make way for the more appropriate name.

Raw Materials of Nitroglycerin Manufacture. The materials used in making nitroglycerin are nitric acid, sulphuric acid, and glycerin. The reason for employing sulphuric acid here as in the case of nitrocellulose manufacture is to take up the water formed in the reaction, thereby keeping the nitric acid up to its full strength, The glycerin employed is the ordinary glycerin of commerce, obtained as a by-product in the saponification of fats. It has a specific gravity of 1.262, corresponding to 99 per cent of glycerin and 1 per cent of water.

Process of Manufacture. The process of manufacture consists simply in adding the glycerin to the mixed acids (observing suitable precautions), separating the glycerin nitrate from the acid mixture, and purifying it. The methods used in practice for carrying out this simple reaction, however are very diverse, and for full details thereon reference must be had to larger treatises such as O. Guttmann's "Manufacture of Explosives," or Kedesdey's "Sprengstoffe."

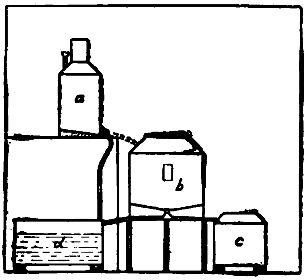

FIG. 330.—Schematic arrangement of nitrating and washing vessels of a nitroglycerin factory.

In principle the arrangement of the apparatus for making nitroglycerin may be seen from the accompanying diagram, Fig. 330. In this diagram *a* is the nitrating vessel in which the glycerin is brought into contact with the mixed acids. It is provided with a thermometer, a coil for cooling and a device for stirring the mixture. This device may consist of either a mechanical stirrer, or an inlet for compressed air. *b* is a tank into which the contents of the nitrating vessel are discharged and allowed to remain until the nitroglycerin has separated from the acids. Being of a

lighter specific gravity than the mixed acids, the nitroglycerin collects at the top. *c* is a vessel into which the separated nitroglycerin is drawn and given a first washing to remove most of the adhering acids. *d* is a safety tank full of water into which the contents of *a* or *b* may be dumped whenever it appears to the workman in charge that the nitroglycerin contained in these vessels is about to decompose with violence. The probability of such a contingency is observed by a sudden rise in temperature and the appearance of dense red fumes. When the nitrating mixture gives such indications prompt action is necessary to save life and property.

FIG. 331.—Nitrating vessel of a small dynamite factory.

According to the equation given above, 2.15 parts of nitric acid (95 per cent strength) is sufficient for complete nitration of the glycerin. As, however, complete nitration is not attained except in the presence of an excess of nitric acid, and not then except in the presence of much sulphuric acid, it is usual to employ the following proportions: glycerin, 1 part; nitric acid, 2.8 to 3 parts, and sulphuric acid 4.6 to 4.8 parts. The yield of nitroglycerin may be increased by adding more nitric acid, but in general the theoretical yield is never reached. According to the relative prices of glycerin and nitric acid the proportions of these materials may be varied to conform to the limits of economical production.

Fig. 331 shows the nitrator, and Fig. 332 the washing vessels of a small plant for nitrating glycerin. This plant will use for one charge 4000 pounds of a mixed acid consisting of

35.5 per cent of nitric acid;
62 per cent sulphuric acid;
2.5 per cent of water;

into which is run 635 pounds of glycerin, the temperature during this operation being maintained at about 65° F. The run should be com-

Fig. 332.—Tanks in which nitroglycerine is washed.

pleted in less than forty minutes. Under present conditions, these materials will yield 1400 pounds of nitroglycerin.

The nitroglycerin after separation from the acid is first washed twice with small amounts of water, using compressed air for the mixing. It is then washed with a weak solution (not exceeding 1 per cent) of sodium carbonate, this salt being added to the wash water a little at a time. The object of using the sodium carbonate is to neutralize the acid which may not have been removed by the wash water. This treatment is then followed by a thorough washing with pure water at a temperature below 90° F. to remove the alkali, no trace of which should remain. The point at which the washing may be regarded as complete is recognized

by the potassium iodide-starch test, as described under nitrocellulose. In this test no iodine should be liberated within twenty minutes at a temperature of 170° F., otherwise the washing must be continued until a satisfactory test has been obtained.

Dynamite. Nitroglycerin is a heavy oily liquid and in this form has but a limited applicability. For convenience in use it must be put into a form wherein it may be easily handled. This is done by causing it to be absorbed by various porous bodies, such as infusorial earth, or kieselguhr, which can be made to absorb three times its weight of nitroglycerin. Such a mixture of nitroglycerin and kieselguhr forms an earthy, friable mass, which can be loaded into paraffined paper cartridges and is sold under the name of 75 per cent dynamite, or No. 1 giant powder. This is the original dynamite as manufactured by its inventor, Nobel.

A disadvantage of kieselguhr dynamite is that it contains 25 per cent or more of its weight of inert matter, whereby its strength as an explosive is correspondingly reduced. On this account the original dynamite has been improved by the choice of other absorbent agents. The dynamite now mostly used consists of 15 per cent of wood pulp (sometimes partly nitrated), 33 per cent of nitroglycerin and 55 per cent of sodium nitrate or ammonium nitrate. The wood pulp serves to absorb the nitroglycerin, but this, as in the case of kieselguhr, means the introduction of an inert material into the explosive. The wood pulp, however, unlike the kieselguhr, contains carbon and hydrogen, which can combine explosively with oxygen under appropriate conditions. These conditions are supplied by the presence of sodium nitrate, which here serves the same purpose of oxygen carrier as does potassium nitrate in black powder.

Dynamites are generally classified according to the amount of nitroglycerin content. Thus, a 50 per cent dynamite means a dynamite containing 50 per cent of nitroglycerin.

Gelatin Dynamite. Nitroglycerin has the property of dissolving nitrocellulose to a limited extent. A mixture of approximately 9 parts of nitroglycerin and 1 part of nitrocellulose forms a clear, jelly-like mass containing no inert matter, which constitutes a powerful explosive. The name gelatin dynamite is applied to this product on account of its jelly-like consistency, and not because it contains gelatin.

Low Freezing Dynamites. An undesirable property of nitroglycerin, whether alone or mixed with inert substances, is that it solidifies at comparatively mild temperatures. When so frozen it is less sensitive to shock and is less apt to be completely exploded when set off in a blast. For this reason frozen dynamite must be thawed out before use. Much attention has been devoted to attempts to obviate this inconvenience, and in recent times these efforts have resulted in various new modifications of dynamite. The most direct treatment is to add some substance, such as mononitrobenzene or dinitrobenzene to the nitroglycerin with the object of reducing its freezing point. More satisfactory results have

been obtained by the manufacture of other nitration products of glycerin. Of these may be mentioned the following:

Dinitroglycerin. This is made by adding 10 parts of glycerin (specific gravity 1.262), with cooling, to 33 parts of nitric acid (specific gravity 1.50). The dinitroglycerin is recovered from this mixture by di uting with water. While the freezing point of nitroglycerin is +11° C., that of dinitroglycerin is −57° C. In possessing such a low freezing point, dinitroglycerin has a distinct advantage over trinitroglycerin, although it is not without certain other disadvantages besides being somewhat less powerful as an explosive.

Tetranitrodiglycerin. When glycerin is boiled for some time there is formed a substance known as diglycerin, which consists of two molecules of glycerin minus one molecule of water. This diglycerin can be nitrated like glycerin. The resulting tetranitrate also has a low freezing point. Nitration of a mixture of glycerin and diglycerin also gives a means of making low-freezing dynamites.

Dinitromonochlorhydrin is obtained by nitrating monochlorhydrin, $C_3H_5(OH)_2Cl$. An addition of 30 per cent of dinitromonochlorhydrin to nitroglycerin makes the resulting mixture practically unfreezable. On account of the presence of chlorine in this substance explosives containing it cannot be used in mines, or other closed spaces, as it makes the air irrespirable.

Other substances which have been used in the manufacture of low-freezing dynamites are dinitroacetin, which is the acetic ester of dinitroglycerin and dinitroformine, which is the formic ester of the same substance.

Aromatic Nitro-compounds used as Explosives. Chief among these is picric acid, $C_6H_2(OH)(NO_2)_3$ which is the trinitro derivative of phenol (carbolic acid). It is made by heating equal parts of phenol and sulphuric acid at 100–120° C., until the two substances have united to form phenol-sulphuric acid. This product is then dissolved in double its weight of water, the mixture being then poured into concentrated nitric acid. The resulting picric acid is separated in centrifuges. Picric acid, either as such or in the form of its ammonium salt, is used as a bursting charge in armor-piercing shells for guns of high calibre. The famous "shimose" of the Japanese is simply picric acid in compact form, obtained by melting and pouring into the shell. The reason for employing picric acid in shells is that besides having certain other desirable properties, it is the most powerful explosive known.

Picric acid, although a very powerful explosive cannot be set off except through shock produced by special means. Its salts, other than the ammonium salt, are much more easily exploded than the acid itself.

Trinitrotoluol is also much used as a high explosive for military purposes. Trinitrobenzol, trinitroanisol and other substances of similar constitution, have been used for the same purpose. Picric acid and trinitrotoluol are

used to a limited extent as industrial explosives, but are considered too expensive for general use.

Fulminants or Detonators. Explosives may be divided into two general classes according to the means required to set them off or bring about their decomposition with explosive effect. The first class includes those which are set off by simple ignition. To this class belong black powder and nitrocellulose When a lighted match is applied to black powder, the part first heated begins to burn with great rapidity, the combustion being supported by the materials contained in the explosive itself, i.e., there is induced a chemical action between the potassium nitrate on the one hand and the carbon and sulphur on the other. The resulting process of combustion is rapidly propagated throughout the mass and there is suddenly produced a large volume of hot gas with an enormous expansive force. Comparatively speaking, however, the wave of combustion in black powder travels at a low speed. The force of the explosion, therefore, develops slowly and its rate of development is easily capable of measurement.

The second class of explosives here considered are those whose explosive effects are not developed by mere ignition Dynamite and picric acid, for example, when set on fire under certain conditions merely burn, without necessarily producing an explosive effect. If, however, picric acid or nitroglycerin (and under certain conditions, nitrocellulose also), be confined in a small space and struck a sharp blow, there is set up an explosive wave of decomposition, distinct from the wave of combustion, the difference between the two being that the former is propagated with practically immeasurable velocity. In order to bring about the maximum effect of such an explosive, it is therefore necessary to induce an explosive wave in its mass, and this in practice is accomplished by the use of a "priming charge," consisting of a small amount of some explosive which decomposes with extraordinary velocity. Such primers are the salts of fulminic acid, the most important being mercury fulminate. So great is the rate of decomposition of this substance when heated or struck that the expansion of the evolved gas has the effect of a blow delivered by a mass moving at a velocity infinitely great. The shock so produced against the adjacent mass of picric acid or similar body is translated into a wave of decomposition, which instantaneously transforms it into gaseous products.

Mercury fulminate can be made to set off black powder and all other explosive mixtures. It is used in the form of caps or detonators n practically every instance where an explosion is to be brought about, whether for industrial, sporting, or military purposes. All shells used in modern warfare carry special detonators of mercury fulminate for setting off their bursting charges.

Mercury fulminate is made by dissolving mercury in nitric acid in the presence of alcohol. Its manufacture and handling are very dangerous.

XLI

LEATHER

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WHEN the pelts of animals are allowed to remain moist they soon putrefy, while if dried they become hard and horny. To obviate these conditions, certain processes known as tanning are employed. The object of this treatment is to convert the putrescible animal matter into a material which is permanent, and at the same time possessing sufficient softness or flexibility for the purposes for which it is intended. As these range from heavy sole leather to light kid, there are wide divergences in the processes employed, materials used, and the methods of their application.

Structure of the Skin. The skins of the various animals at first glance seem to have very little in common; on closer examination, however, it will be seen that they all have a similar structure, though on account of the difference in texture and thickness their practical application differs very greatly. The skins of lizards, alligators, fishes and serpents differ from the higher animals in that the epidermis becomes harder and forms scales.

The skin is not merely a covering for the animal, but is at the same time the seat of the organs of sense and produces certain important secretions. It consists of two principal layers, the *epidermis* (*epithelium, cuticle*) and the *corium* (*derma, cutis,* or true skin). The *epidermis* is very thin as compared with the true skin which it covers, and is entirely removed preparatory to tanning; it nevertheless possesses important functions. Its inner mucous layer, which rests upon the true skin, is soft, and composed of living nucleated cells, which multiply by division and form cell-walls of *keratin.* These are elongated in the deeper layers, and gradually become flattened as they approach the surface, where they dry up, and form the horny layer. This last is being constantly worn away, thrown off as dead scales of skin, and as constantly renewed from below, by the multiplication of the cells.

It is from the epithelial layer that the hair, as well as the sweat and fat glands, are developed. Each hair is surrounded by a sheath which is continuous with the epidermis, and in which the young hair usually

grows as the old one falls out. Near the openings of the hair-sheath upon the surface of the skin the ducts of the sebaceous or fat glands pass into the sheath and secrete a sort of oil to lubricate the hair. The base of the hair is a bulb, enclosing the hair papilla, which is a projecting knob of the true skin and which by means of the blood-vessels contained in it supplies nourishment to the hair. The hair bulb is composed of round soft cells, which multiply rapidly, and pressing upward through the hair sheath, become hardened, thus increasing the length of the hair.

The process of development of the sudoriferous or sweat glands is very similar to that of the hair. They consist of more or less convoluted tubes with walls formed of longitudinal fibers of connective tissue of the corium, lined with a single layer of large nucleated cells, which secrete the perspiration.

Besides the hair, and hair-sheaths, and the sebaceous and sudoriferous glands, the epidermis layer produces other structures of a horny character, including horns, claws, and nails; which both chemically and anatomically are analogous to exaggerated hairs. This is apparent in the quills of the porcupine. The whole of the epidermis, together with the hairs, is separated from the corium by an exceedingly fine membrane, called the *hyaline* or glassy layer. This forms the very thin *grain* surface of tanned leather, which is of a structure different from the rest of the corium.

The structure of the corium or true skin is quite different from that of the epidermis. It is composed principally of interlacing bundles of fibers, known as *connective tissue*, which are cemented together by a substance more soluble than the fibers themselves. These fiber-bundles are more loosely interwoven in the middle portion of the skin, but become compact again near the flesh. The outermost layer, just beneath the epidermis, is also very close and compact. The skin is united to the animal by a network of connective tissue (*panniculus adiposus*), which is frequently full of fat cells, and is then called adipose tissue. This portion, together with some actual flesh, is removed in the process of *fleshing*.

Ordinarily the corium or true skin is the only portion which is used in the production of leather. In order to obtain it in a suitable condition for the various tanning processes, the hair or wool, together with the epithelium, must be completely removed without damaging the skin itself; and especial care must be taken that the grain, or portion next the epidermis, does not suffer injury during the treatment.

Classification of Pelts. The pelts of animals come to the tanner in three conditions as *green* (fresh from the animal), *salted* (where salt has been rubbed on the flesh side), or *dried* (usually stretched on boards in the sun). The pelts so received are divided according to their size into three general classes, namely: *hides*, comprising the skins from large and fully grown animals, such as the cow, horse, camel, walrus. These form thick heavy leather, used for shoe soles, machinery belting, and other purposes where stiffness and strength, combined with wearing qualities

are necessary. They are also cut into splits for use as shoe uppers, bag and case leather, automobile and carriage tops, furniture and upholstering. *Kips* are the skins of undersized animals of the above species. *Skins* are obtained from small animals, such as calves, sheep and goats. Kips and skins yield a lighter leather than hides. This is suitable for a great variety of purposes, such as uppers for shoes, pocket books, book bindings, gloves and fancy leather. Pelts vary in thickness and texture in different parts, being thicker on the neck and butt than on the flank and belly. The same species vary greatly, according to climatic conditions under which they are raised, and to their breeding and feed. They often show injury such as cuts, brand marks, and sores caused by the bot-fly or warble. Diseased hides are a source of great danger to the tanner on account of the contagious nature of some of the diseases, especially anthrax.

Soaking. Whether the skins are green, salted, or dried they must first be soaked in water in order to remove the dirt and blood in the case of green skins, salt in the salted skins, and for the purpose of softening in the case of dried skins. It is very essential that the skins should be free from all foreign matter before entering the limes or other unhairing solutions, as the presence of salt greatly retards the plumping; while the presence of albuminous matter is apt to set up an undesirable fermentation in the after treatments. When perfectly soft and well washed the skins are removed from the *soaks*, thrown over a rounded beam, tails and ear-laps trimmed, and any adhering portions of flesh removed.

The time of soaking varies from one or two days to several weeks, depending upon the thickness of the hide and the age and temperature of the soak. Putrid soaks soften much quicker than fresh ones; but great care is necessary in using them lest the decomposition attack the hide fiber itself. For heavy hides which soften very slowly it is found to be of advantage to run in a drum for a short time with water at a temperature of about 40° F., the tumbling movement thus materially aiding in the softening process.

Water for Tannery Purposes. Water is used in the tannery for soaking and washing, for making limes, for preparing bates or puers, for the leaching of barks and the solution of extracts, for steam boilers, and in dyeing. For all of these purposes it is evident that the water should be as pure as possible. Either the tannery must be located in a section where a good water supply is available, or chemical means must be used to soften it. The most objectionable features of a bad water supply are its temporary and permanent hardness. These may both be removed by treating with a proper softening agent, such as sodium carbonate. The treatment should be carried out in tanks and the sludge allowed to settle before use. A small amount of hardness is not harmful, however, and up to ten parts of solids per hundred thousand it may be disregarded. Water possessing temporary hardness will cause the following objection-

able conditions. When employed for leaching the calcium and magnesium carbonates in it combine with the tanning to form an insoluble substance which has no tanning properties. In dissolving basic dyes with this kind of water there is a precipitation of the color base, thus rendering part of the dye useless. Further, as this precipitate is deposited on the skin it causes uneven dyeing and gives rise to spots and streaks.

Permanent hardness is very objectionable when employed for boiler purposes, but otherwise is not so harmful as temporary hardness. The presence of calcium and magnesium sulphates is usually the cause of permanent hardness, and these salts being already combined with a strong acid can have no action upon the tannic acid during the process of leaching. There might possibly be a slight tendency to lessen the solubility of the tannings, however, but this could be overcome by softening in the case of water with a high degree of hardness. One danger in using a water containing calcium and magnesium sulphates arises during the process of scouring and fat-liquoring, as one part of lime reckoned as carbonate destroys twelve parts of soap, producing a sticky and insoluble lime soap which adheres to the fiber, and is very difficult to remove.

Mud under any circumstances is objectionable, as it usually contains organisms which encourage the putrefaction of hides during the soaking process. It also almost always holds iron, which either produces stains or gives a dark-colored leather. Sodium sulphate is probably inoperative. Sodium chloride, on the other hand, prevents plumping, and may be the cause of thin and soft leather, and in large amounts will greatly impede the proper exhaustion of many tanning materials.

Depilation. By the term depilation is meant the removing of the hair and epidermis. This is necessary in all kinds of leather, except that to be used for furs. The former method of accomplishing this was by means of incipient putrefaction. In this case the soft mucous matter of the epidermis became affected, thus loosening the hair without materially injuring the true skin. This method is still employed by many tanners of sole leather, and is called *sweating*. The operation is carried out in closed rooms, which are kept at a temperature of about 70° F. The hides are hung in the *sweat pit*, in small chambers holding about 100 hides each. A large quantity of ammonia is given off during the decomposition, which aids in the solution of the epidermis and the loosening of the hair. After four to six days of this treatment, the hair is sufficiently loosened tc be removed by working over the beam with a blunt knife made for this purpose. Hides which have been unhaired in this way are soft and *fallen* and must first be swollen by running in an acid liquor before entering the tanyard. This treatment is especially necessary in the case of sole leather. However carefully this operation is conducted, there is liability that the putrefaction attack the skin itself, thus causing a weak grain; for this reason it is used less and less each year.

Liming. Lime is the agent generally employed for unhairing, although it also has its disadvantages. In preparing the lime solution a quantity of fresh lime (calcium oxide) is slaked by placing in a shallow tank, similar to that used by builders, and adding sufficient water to thoroughly moisten it. At the end of one or two hours it becomes heated and falls to a powder. Sufficient water is added to form a thick paste, in which condition it may be kept for several weeks or even months without much change. When required for use a suitable amount is dug out, stirred with water to remove rocks, and then run into the pits. As only the lime in solution is available for unhairing the addition of a large excess is unnecessary. It is essential simply to provide a surplus of solid lime to replace that taken up by the hide. It is impossible to set any fast rule as to the quantity of lime to use, but a safe margin is 10 pounds of lime for each 100 pounds of hide.

The usual method of liming is to lay the hides one at a time in the lime solution, taking care that each hide is well immersed before entering the next one. The hides are taken out (*hauled*) each day and the liquor well *plunged up*, in order to distribute the undissolved lime throughout the pit. They are then thrown back (*set*), care being taken to see that they are fully spread out. In some tanyards the hides are joined by hooks (*toggled*) and reeled from one pit to another, or to the same pit. Sometimes hides are suspended in the liquor, and by means of a paddle, or by blowing in air, the limes are kept in motion. The most common method, however, where it is desired to agitate the liquor, is to employ the ordinary paddle box and run it at intervals during the day.

The action of lime on the hide is to swell up and soften the epidermis cells, dissolve the mucous layer and loosen the hair so that on scraping with a blunt knife, both the epidermis and hair are easily removed. The action on the true skin is very vigorous, causing the hide to become plump and swollen, and, at the same time dissolving the cementing material of the fibers, thus causing them to become split up into finer fibrils. This swelling is probably caused by the formation of a lime soap, due to the union of the lime with the fatty matter of the hide. Not only does the liming process remove the hair and epidermis, but it also is of value in the fleshing process, as it gives to the hide a greater firmness, which is very desirable when working with the knife or on the machine. The time of liming varies with the season of the year, with the kind of skins treated, and may run from three to fifteen days. The age of the lime has a great influence on the time of treatment as well as on the character of the finished product. Old limes unhair much quicker than fresh ones. It is often customary to place the hides in an old lime for several days, or until the hair and epidermis have started to loosen, then change them to a fresh lime, which produces the desired plumping of the fibers. Great care, however, must be taken that the limes do not become too old; as this condition will be very apt, especially in hot

weather, to produce a transparent swelling of the tissue with destruction to the fiber.

Sulphide of Arsenic. When the *red sulphide of arsenic*, As_2S_2, is dissolved in hot water and added to lime it increases its depilating effect. It is employed especially in fine leathers, to which it gives the necessary stretch, softness, and clearness of grain, without the loss of hide-substance and the loosening effect caused by ordinary liming. The amount used varies somewhat, but may be said to run from 0.1 to 0.4 per cent of realgar and 4 to 6 per cent of lime, reckoned on the weight of the green skins.

Sodium Sulphide. This substance when employed in strong solution, 5 per cent or over, has the effect of rapidly reducing the hair and epidermis to a sort of pulp, which may be easily swept off with a broom, or even washed off in the drum. The operation is usually conducted in a paddle, and takes about two hours for the complete removal of the hair and epidermis. The action on the hide-substance, and especially upon the cementing material, is very slight, although the grain is swollen and temporarily rendered somewhat tender. As this strong solution destroys the hair it is only used on such stock as goat skins, where the hair is of minor importance. On the other hand, when used in weak solutions, 0.25 per cent or less, in conjunction with lime, the hair is but little injured, the hair-roots and dirt being rapidly loosened with a result somewhat similar to that produced by arsenic sulphide.

Calcium Sulphydrate. This compound is a very powerful depilatory, but is not used to any extent on account of its unstable character. It is probably formed to some extent when sodium sulphide and arsenic sulphide are added to lime. It may be produced by passing hydrogen sulphide into milk of lime until the latter becomes saturated. This is the substance largely sold as a patent depilatory for removing superfluous growths of hair.

Fig. 333.—Unhairing Machine.[1]

Unhairing. When the process of depilation is complete the skins or hides are removed from the pits and allowed to drain for half an hour or more. They are then placed on the beam and the hair removed as described under the sweating process. In recent years various machines have been devised to accomplish the removal of the hair, and these have been brought to such perfection that the old method of hand work has been almost entirely

[1] Turner Tanning Machinery Co., Peabody, Mass.

eliminated in the modern tannery. The unhairing machine (Fig. 333) is provided with a spiral, blunt knife which revolves on a rubber roller.

Fleshing. After being unhaired, the skins are next *fleshed*. This operation is for the purpose of removing any fat or flesh which has been left on the pelt by the butcher, and consists in working the hide over a beam in a somewhat similar manner to that described for unhairing, except that the knife employed is heavier and is sharp on both sides. In nearly all modern tanneries, however, the beam has been displaced by machines (Fig. 334) for the purpose.

Fig. 334.—Fleshing Machine.[1]

The type of machine employed for fleshing skins differs somewhat from that used for hides, although the operation is similar in each. The essential feature of the machine consists in a cylinder provided with spiral blades, which are arranged right handed on one side, and left handed on the other. By means of this kind of blade the flesh is easily removed, and the hide stretched in all directions.

Bating. It is very essential that the lime, or other depilating agent, should be completely removed when it has done its work, since its action is very harmful when brought in contact with tanning materials. The presence of lime also has a tendency to weaken the fiber and to produce a harsh-feeling product as well as to cause a loss in the materials employed in the currying and finishing processes. For most leather it is not only necessary that the lime be completely removed, but that the skin should be brought from its swollen to a soft and open condition. To accomplish this with the heavier classes of dressing leather, such as split hides, kips, colt and calfskins, the stock is run into a weak fermenting infusion of pigeon- or hen-manure. The time of immersion depends upon the strength of the liquor and upon the nature of the pelts under treatment.

[1] Turner Tanning Machinery Co., Peabody, Mass.

Puering is a very similar process, applied to the finer and lighter skins, such as glove- and glacé-kids and moroccos, in which dog-manure is substituted for that of birds. As the mixture is used warm and the skins are thin, the process is complete in a few hours. Neither bating or puering are very effective in removing lime, but seem to act upon the hide substance by means of bacterial products, causing the pelt to fall, that is, to become soft and flaccid. Great care must be exercised in this treatment, in order to prevent possible decomposition of the hide, or what is known as "running of the grain," that is, if the action becomes local and the grain is eaten away in spots. During electrical storms the action becomes very much intensified, and may result in a complete decomposition of the pack, unless the skins are drawn out or the liquor greatly diluted.

When the skins are removed from the dung infusion, they are slightly alkaline in reaction from excess of lime and ammonia, which must be removed before they are ready for the actual tanning process. The neutralization is accomplished in various ways, and is known as *drenching* and *pickling*.

Drenching. Drenching is sometimes used as a substitute for bating with calfskins, but usually follows the bating process. It not only serves to remove the lime completely, but tends to slightly plump the skins. The drench liquor is prepared by allowing an infusion of bran in warm water to ferment under the action of special bacteria which develop lactic and acetic acids. When a bath is once prepared it can be used continuously by drawing off part of the liquor, and adding fresh portions of bran and water. In neutralizing by this method the skins are entered, and the liquor moved occasionally to get a uniform contact. As fermentation becomes well established, during the night, the skins will rise to the top, on account of the gas produced. The night watchman then forces them under again, by means of a heavy pole. On rising a second time they are free from lime, and in a soft and open condition. This open condition is very essential in soft leather, but is not desirable in harness, or other kinds of firm and heavy leather.

Pickling. This method usually consists in drumming the skins in a concentrated salt solution to which a small amount of sulphuric acid is added. The ratio between salt and acid is usually 8 pounds of salt to 1 pound of acid. The solution should stand 1.060 sp.gr. (8° Bé., 12° Tw., 60° Bk.). In some tanneries the pickling is carried out in the paddle, and fresh acid introduced after each pack has been removed. If the pickle has the correct acid strength 15 c.c. of normal sodium hydroxide will neutralize 100 c.c. of the liquor, using phenolphthalein as an indicator. The salt should be replenished by adding a sufficient amount to keep the specific gravity up to 1.060. The usual practice in this country is to pickle in the drum, which has the advantage of being more rapid and does not depend upon chemical control.

For certain grades of leather the use of lactic acid or of formic acid

has been found to give very satisfactory results. Each of these are very active deliming agents. Ammonium chloride has a solvent action upon the lime and is used in many of the patent bates. Boric acid is rather widely employed, as it not only has the power of removing the depilating agent, but hastens the tannage, gives a good color and a smooth grain.

In all of the processes where chemicals only are employed the results obtained are different from that when bacterial bates are used.

In certain kinds of leather it is desirable to get a smooth grain, combined with a soft and open condition. This can be best secured by the use of manure, or some of the more recent bates which depend upon bacterial fermentation for their peculiar property. Among the manure substitutes may be mentioned " Dermiformer," which is prepared from sour milk with the proper ferment. This substance is used in the same manner as manure, and like a manure bate it gives the best results in a warm solution (90° F.). " Puerine " is much used in this country, and may be employed alone or in combination with manure. " Oropon " is a form of bacterial bate which has recently come upon the market, and has many good points which should commend it to the tanner. The " Oakes Process " is especially applicable where a smooth grain with a soft and open condition is desired. It depends upon the fermentation of glucose in the presence of sulphur. The bate is prepared at a temperature of 95° F. with 5 per cent of glucose, $\frac{1}{2}$ per cent of sulphur, and 1 pound of yeast for every 1000 lbs. of hides taken. In starting the bath it should be allowed to stand for twenty-four hours before the first pack is entered. Once under way it may be used continuously by drawing off about one-quarter of the solution and adding one-half of the original amount of glucose sulphur and yeast.

The Tanning Operation. The term " tanning " originally was applied to the treatment of hides and skins with some vegetable product containing tannic acid. With the introduction of chemical methods for preserving the hide substance the old term has still been retained; so that the process of tanning may mean either a treatment with mineral salts, oils, or aldehydes, as well as those methods in which vegetable substances containing tannic acid are employed.

Vegetable Tannage. For the actual tanning operation, the liquor used depends entirely upon the nature of the skins or hides, and upon the kind of leather it is desired to produce. There are three general methods, however, which are in common use. The first method consists in suspending the stock in a solution of the tanning material. The second method is carried out in a paddle so that the stock is kept in constant motion during the whole or part of the operation. The third method consists in tumbling the stock in a drum or pin mill during the whole or part of the operation. In the heavy hides the time of treatment is of course very much longer than is the case with light skins.

Belt, Sole and Harness Leather. The hides as they come from the "beam house" are run in an acid liquor in order to neutralize the lime, and to bring them to a plump or swollen condition. They are then transferred to the *stick pits* or *suspenders;* the name coming from the fact that the hides are suspended by the butts from sticks placed across the pit. The liquor in the first pit is very dilute, and nearly exhausted, having a density of about 10° Bk. From day to day the liquor is changed, so that a gradual increase in its strength is obtained. After the hides have remained in the suspenders from eight to ten days they are laid in pits called *handlers*, where a stronger liquor is employed. The weakest liquor from the youngest handler pit is run daily to the suspenders, a new and stronger liquor being run into the pit holding the oldest and most tanned pack. As this pack is removed the next in age takes its place, while the youngest pack enters the pit containing the weakest liquor. In this manner each pack receives a change of liquor of graduated strength, passing from about 20° Bk. to one of 40° Bk. In the handlers the hides are completely struck through or tanned and then pass to the *layers.*

In the layers the hides are spread out as smoothly as possible and dusted with ground bark; and are piled up alternating a layer of hides with a layer of bark. When the pit is full concentrated liquor is run in until the pack is completely covered. The hides are allowed to remain undisturbed in this condition for several weeks, or until they have taken up as much as possible of the tannic acid and other material.

Scouring. On removal from the layers the stock is thoroughly washed to free it from insoluble matter, and then *scoured* to remove the "bloom." The scouring or cleaning process is accomplished by placing the hides on the movable table of the scouring machine, where they are violently scrubbed with a coarse brush and stone slicker, while a stream of water is allowed to play over the surface.

Bleaching and Retanning. In order to secure a better and more uniform color it is customary to "strip" or remove a part of the surface tannage by means of borax or weak alkali. This is usually carried out in the drum, and the excess of alkali neutralized with oxalic, sulphuric, lactic, or formic acids and thoroughly washed. The cleared hides are then retanned with sumac or other light-colored tanning material. Previous to the retanning it is also customary, in most shops, to remove a small skiver from the flesh-side so that the hides will have a uniform thickness and similar appearance.

Stuffing. The object of this operation is to surround the fibers with fat and oil, which serves to lubricate them and render the leather more pliable, while at the same time it gives to the stock more body or weight. The process most commonly employed consists in placing the *sammied* (damp) hides in a drum, heated to about 140° F. and running in the melted stuffing material through the trunnion. Many kinds of stuffing greases are used. One which gives very satisfactory results consists of a mixture of tallow and cod oil. After running for about half an hour the hides

are removed and set out while in a warm condition. This setting out is accomplished on a machine similar to that described under *fleshing*. In the setting out the excess of grease is removed and the stock given a mild stretching treatment.

Framing. From the setting-out machine the hides are placed on frames, where they are given as much of a stretch as possible and allowed to dry in a state of tension.

Finishing. On removal from the frames the hides are given a coat of wax, shellac, gelatin, blood albumen or other finishing substance and after rolling on the *jack* are ready for the market.

In the tanning of heavy leather the above treatment is sometimes varied by cutting the hides into " bends " and " bellies "; or into " butts " and " shoulders." The subsequent treatment is somewhat modified for the different portions. The tanning materials used for heavy leather vary, consisting either of one or several tanning products. The density of the liquor employed may also vary within rather wide limits.

Vegetable-tanned Calfskins. In preparing calfskins for the tanning process they should be well beamed and bated until they are soft and open. The washed skins are then suspended on sticks and allowed to hang in the tan liquor as described under hides. The strength of the liquor, however, may be somewhat changed, although 8° Bk. is very satisfactory at the start. The strength is increased uniformly for six days when the stock should be completely struck through or tanned. The skins are then removed from the suspenders, washed and horsed up to drain. When in the proper *sammied* condition they are shaved and retanned in sumac, to which a small amount of sulphurous acid, oxalic acid, formic acid, or formaldehyde is added. The retanning may be carried out in a drum, but it is preferable to employ the paddle. When the retanning is complete the skins are again washed, treated with about 3 per cent of soluble oil, set out, and tacked on frames to dry. Having thoroughly dried they are removed from the boards, and are ready for the coloring operation.

Vegetable-tanned Sheepskins. Sheepskins come to the tanner in the pickled condition containing sulphuric acid and salt. They are usually washed free from the pickle with a strong salt solution before they enter the tan liquor. These skins may be tanned in pits as described for calfskins, except that it is necessary to have a certain amount of salt in the solution. The tanning may also be carried out in the paddle.

A very rapid method for tanning sheepskins and *skivers* (split sheepskins) consists in running the stock, without removing the pickle, in a drum with 25 per cent of solid quebracho extract, or its equivalent of other tanning material, and 10 per cent of salt. The time necessary in this method is about one and one-half hours. When the skins are tanned they are thoroughly washed and hung up to dry. As sheepskins contain a large amount of fat they should be degreased before the coloring and finishing operations. This is accomplished by dipping in naphtha. If

it is not convenient to give them the naphtha treatment they may be run in a drum with ½ per cent of soda ash, washed, the alkali neutralized with sulphuric or formic acid, and washed again. When dry the skins are buffed on the emery wheel, retanned and colored.

Vegetable-tanned Goatskins. At the present time practically all of the goatskins are tanned by the two-bath chrome process. For certain kinds of fancy morocco leather, however, sumac or other vegetable tanning material is employed. The bating of goat skins is more difficult than other pelts and a more active substance has to be employed.

Chrome Tannage. The action of chromium salts upon hide substance was first studied by Knapp in 1858, but his investigations led him to conclude that their application was of no practical value. Although other investigators took up the matter, it was not until 1884 that any really important advance was made. At this time Augustus Schultz patented his "two-bath process." In this process the skins or hides are treated with a solution of chromic acid, produced by the action of hydrochloric acid upon sodium or potassium dichromate and afterward with a solution of sodium thiosulphate and hydrochloric acid. The hide substance takes up the chromic acid, which is subsequently converted to the basic condition by means of the "hypo." In 1893 Martin Dennis made a study of the action of chromium salts as previously investigated by Knapp, and perfected a method of "one-bath tannage," on which he was granted numerous patents.

Two-bath Chrome Process. While the details involved in the application of this process vary, yet chrome tanning is uniformly carried out either in a paddle or drum. Different kinds of leather require different percentages of the chemicals. In the drum tannage 6 per cent sodium or potassium dichromate and 3 per cent of hydrochloric acid, regulated on the weight of the wet skins, are dissolved in sufficient water for the proper handling of the stock. The skins or hides are placed in the drum and the chrome solution added, the drum being kept in motion. The hides or skins are worked in the solution until they have taken on a uniform yellow color which has completely struck through. They are now removed from the drum and freed from the superfluous liquor by horsing up over night, or by putting out; the latter operation may be done by hand or on the machine. After standing for twenty-four hours the chromed stock is returned to the drum, and run for about one and one-half hours with a solution of 12 per cent of sodium thiosulphate and 6 per cent of hydrochloric acid. On removing from the drum the stock should have a blue-green color and be uniform throughout. If thoroughly tanned no curling will occur when a strip is placed in boiling water. On removing from the drum the stock is horsed up for twenty-four hours to allow the chrome to set, neutralized by running for half an hour in a ½ per cent sodium bicarbonate solution, washed in running water for half an hour, horsed up, and allowed to drain.

The reactions which take place in this process are represented in the following equation:

$$Na_2Cr_2O_7 + 2HCl = 2NaCl + 2CrO_3 + H_2O.$$

The CrO_3 produced combines with the gelatine, forming a compound with it. The sodium thiosulphate now acts as a reducing agent upon the chromic oxide, converting it from the acid to the basic condition, the reaction taking place in two stages:

1. $2CrO_3 + 6HCl + 3Na_2S_2O_3 = 3Na_2SO_4 + 3S + Cr_2Cl_6 + 3H_2O.$

2. $Cr_2Cl_6 + Na_2S_2O_3 + H_2O = Cr_2(OH)_2Cl_4 + SO_2 + S + 2NaCl.$

The basic chloride of chromium held by the fiber is probably converted to $Cr_2(OH)_6$ by the action of the sodium bicarbonate used in washing.

One-bath Chrome. In this process the skins or hides, after coming from the puer, are washed in running water and run in a pickle for about one hour. The pickle is made by dissolving 8 lbs. of salt and 2 lbs. of sulphate of aluminium in a small amount of water, adding 1 lb. of sulphuric acid, and making up to a density of 40 Bk. The object of this treatment is to neutralize any alkalinity of the puer or lime that may remain, and to ensure the stock being in an acid condition before it enters the tan.

Many methods for preparing a one-bath chrome liquor are in vogue. A very good liquor may be made by dissolving 10 lbs. of sodium dichromate in 10 gallons of water, adding 6 lbs. of syrup glucose (40 Bé.), and then very *slowly* introducing 10 lbs. of concentrated sulphuric acid. A wooden vessel may be used for making up this liquor. A less violent action, however, is produced by adding the glucose last, but in this case stoneware or other acid-resisting vessels, must be employed. A liquor when prepared as above and diluted to 45 Bé. will give a product of such strength that 15 lbs. will be required for each 100 lbs. of pickled skins treated.

In using this method the necessary amount of reduced liquor (15 per cent of above liquor, equivalent to 4 per cent of dichrome) is dissolved in a sufficient quantity of water for proper handling of the stock, and 5 per cent of sodium sulphate added to the solution. The pickled skins are placed in the drum, the door closed, and one-third of the solution introduced, while the drum is in motion. At the end of fifteen minutes another third is added, and in thirty minutes the remainder. One-half hour after the last portion has been added ½ per cent of sodium bicarbonate in solution is introduced, and the stock run for fifteen minutes longer. The hides or skins are then removed from the drum, horsed up over night, neutralized with ½ per cent of sodium bicarbonate, thoroughly washed, horsed up and allowed to drain.

Chrome tannage by either of the processes given above may also be carried out in the paddle, but in this case the time of treatment is some-

what longer. The advantage of the paddle tannage is that a smoother grain is obtained with less danger of " pip " leather.

Alum Tannage. This process is employed especially for white kid, glove and light-colored leather. There are many ways of applying the alum, and the following description simply serves to illustrate the method. The skins are limed, bated and pickled in the usual manner. The solution necessary for 100 lbs. consists in dissolving 10 lbs. of sulphate of aluminium, and 3 lbs. of salt in 10 gallons of water; a solution of 1½ lbs. of soda ash is then dissolved in 2 gallons of water and added to the aluminium sulphate very slowly, with constant stirring; 30 lbs. of flour is now triturated with some of the solution, added to the original solution and finally 8 lbs. of egg yolk introduced. The skins are drummed in this mixture for one hour, and hung up to dry. After laying in the *crust* (dry condition) for several weeks they are softened and again drummed with the above mixture.

Oil Tannage. The oldest tanning method of which we have any record was that in which the oil, fat and brains of animals were used to preserve the pelts in a soft and non-putrescible condition. The method as at present applied consists in kneading the goods in contact with certain oils and soft fats. As the fibers slowly dry the fats are worked in between them by means of the mechanical treatment which the goods undergo in the *stocks*. Each fiber is, therefore, separated from its neighbor in a non-adherent condition, and at the same time is surrounded by a waterproofing material. Not only are the fibers surrounded by the oil, but at the same time a vigorous oxidation occurs, resulting in the formation of aldehydes and other insoluble oxidation products. The adlehydes produced, by virtue of their chemical activity, unite with the hide fiber, while the insoluble products coat the fibers mechanically. Oil tannage is used in the manufacture of chamois, buff, and buck leathers.

Chamois Leather. The flesh splits from sheepskins are used in the manufacture of this kind of leather. The skins are given a thorough liming of from twelve to fifteen days, drenched, and the superfluous liquor removed by subjecting to hydraulic pressure. They are now drummed for half an hour to equalize the moisture, and transferred to the stocks, one at a time, where cod oil is sprinkled over each skin. In the stocks the goods are worked for four hours, removed to the drying loft, and dried without heat until they assume an opaque condition. They are now resprinkled and restocked for another four hours, this time being dried at 100° F. to a brown color. The stocking and drying are repeated several times, with an increase in the temperature of the *heater* up to about 160° F. On coming from the final drying the skins are packed in a box, covered with matting, and spontaneous heating allowed to continue.

When the oxidation of the leather is complete it is dipped in water at 110° F. for a short time, and then subjected to hydraulic pressure. The heavy grease which is expressed by this treatment is collected and

sold for leather dressing under the name of *degras*. The skins are then washed with a warm sodium carbonate solution, and the wash water neutralized with sulphuric acid, giving what is known as *sod oil*. The skins are next washed with hot water, nourished with cod oil and soft soap for one hour, squeeze rolled and allowed to dry.

Aldehyde Tannage. The use of formaldehyde as a tanning material has recently been brought to the attention of the tanner by the patents of Payne and Pullman, but as yet it has not become widely employed. The leather obtained by this process resembles buff leather. It is very white, however, and needs no bleaching. The future of this method remains to be seen.

Finishing of Dressing Leather. After the leather is tanned by any of the methods given above it must be finished in such a manner as to meet the requirements of the various purposes for which it is to be used. Only a few of the most important operations in the finishing of leather will be given.

Soaking. On removing the dried goods from the boards or drying room they are dipped in water at a temperature of 110° F. and placed in piles or horsed up for some hours until evenly wet through or *sammied*. The goods may also be sammied by dipping in warm water and then covering with damp sawdust. While still another method is to steam the stock gently and run in a drum for a short time.

Shaving. The object of the operation is to bring the leather to uniform

Fig. 335.—Shaving Machine.[1]

thickness, and may be done by hand or by means of the shaving machine. In either case the goods must be damp. The machine which is used for this purpose is shown in Fig. 335. It is fitted with a spiral knife-blade of steel, half of which is right-handed and half left-handed. The leather is placed over a roller, which may be pressed against the cutting end by

[1] Turner Tanning Machinery Co., Peabody, Mass.

pressing on a foot treadle. The knife-blades revolve at a very high rate of speed, and are constantly sharpened by means of an emery wheel.

Splitting. This operation has replaced shaving to quite an extent, especially for side leather, which is now almost uniformly split out of the limes. In this process the leather is sliced parallel to the grain surface, so that the split portions have the same area as the original leather. Among the numerous types of splitting machines in use the "band-knife" type is the most popular. The machine (Fig. 336) consists of an endless double-beveled knife which passes around two pulley wheels, one of which is attached to power. The sammied leather is pushed toward the knife, grain upward, by two feed rollers; the grain split passing over the knife and the flesh split under it. The thickness of the split can be varied

FIG. 336.—Band-knife Splitting Machine.[1]

from one-sixteenth of an inch up to the thickness of the hide, so that in some cases it is possible to obtain as many as five good splits from one hide.

Scouring. The object of this process is to remove the bloom, loose tan and dirt from the surface of the leather. It is effected by means of warm water, sometimes soap and borax being used, with the aid of slickers and brushes, which work over the surface of the leather. The operation is largely carried out by hand, although machines for the purpose are on the market.

Stuffing. The object of the process is to surround this fibers with fats in order to render the leather more pliable and in some cases to give it more body and to waterproof it. This operation may be carried out by hand or in the drum.

Fat-liquoring. This process differs from stuffing in that emulsions of various oils as well as emulsions of soap and oils are employed in place of the heavy fats. In recent years the use of soluble oils (sulphonated oils) has become common. The term fat-liquoring is usually applied to the light kinds of leather, while stuffing is applied to heavy leather.

[1] Turner Tanning Machinery Co., Peabody, Mass.

Coloring. The dyeing of leather has been greatly modified within recent years owing to the introduction of coal-tar colors, although for several shades the old vegetable colors are still in use.

Black on Vegetable-tanned Leather. In producing this color an ammoniacal solution of hematin is prepared and brushed evenly over the surface, being followed by a striker of black iron and copper sulphate. Nigrosine and other coal-tar blacks are being used for the same purpose.

Black on Chrome Leather. The stock, after being shaved, is placed in the drum and run for half an hour with 4 per cent of hematin crystals and ½ per cent of soda ash, the temperature being at 140° F. The plugs are now drawn for the excess of liquor to drain off and a solution of 1 per cent of ferrous sulphate and ½ per cent of copper sulphate introduced through the trunnion. The stock is worked in this striker for fifteen minutes and the excess removed. A solution of 1 per cent of nigrosine is now added and run for fifteen minutes longer. The goods are well washed first in cold water, then in warm water, fat-liquored at 130° F. for one-half hour with 2 per cent of soap, 1 per cent of neatsfoot oil and ½ per cent of degras. On removing from the drum they are set out, given a coat of equal parts of glycerine and water, and after standing for two hours are hung up to dry. They are subsequently staked and tucked.

Colors on Vegetable-tanned Leather. The well scoured and cleaned goods are run for about fifteen minutes in an acid solution of ½ oz. formic acid to each gallon of water. The excess of acid being removed, ½ per cent solution of tartar emetic is introduced and the drum run for fifteen minutes. The excess of tartar emetic is removed, from ½ to 2 per cent of basic color added (should the water be hard a small amount of formic acid may be added) and the stock run for fifteen minutes. The plugs are now removed and the skins or hides given a thorough washing. To render the stock pliable, the goods are fat-liquored with either soap and oil or with soluble oil, horsed up for several hours, set out and tacked up to dry.

Colors on Chrome-tanned Leather. The shaved stock is retanned in gambia or sumac, scoured and then dyed as under the method for vegetable tannage. Recently, however, other methods have come into use, whereby the process of retanning is eliminated. It has been found that some of the alizarine colors give very satisfactory results when applied in the proper manner. Direct colors are also being used with some success, and especially a combination of acid colors with the direct colors.

Staking. As the skins or hides come from the boards they are in a very hard condition, and must be softened before they can be finished. This operation is now carried out on the staking machine, which is shown in Fig. 337. This machine works the leather up by a sort of a kneading motion and at the same time exerts upon it more or less of a stretching action.

Seasoning. After staking the goods they are spread on the table and given a coat of a mixture of flaxseed mucilage and milk, hung up to dry and again staked.

Rolling. After seasoning and restaking the skins or hides are rolled. This operation is carried out on the *rolling jack.* In this machine a steel

Fig. 337.—Staking Machine.[1]

roller passes over a bed in such a manner that a very great pressure is secured, the object being to work out the wrinkles and give a better appearance to the finished product. After rolling the stock is sometimes given a thin coat of oil and is ready for the market.

[1] F. F. Slocomb & Co., Wilmington, Del.

Glazing. To obtain leather with a high finish it is given a coat of egg albumen, blood albumen, or shellac, and then finished on the *glazing jack*. This machine is very similar to the rolling jack, except that a glass cylinder is used in place of the steel roller, the glass sliding over the surface of the leather instead of rolling. (Fig. 338.)

FIG. 338.—Glazing Jack.[1]

Patent Leather. This kind of leather is made by varnishing ordinary leather. The usual method is to first degrease the tanned stock. It is then given a daub coat of boiled linseed oil and lampblack, thinned to the proper consistency with naphtha. The excess of the coating is removed with the slicker and a mixture of linseed oil and guncotton applied. The hides are then baked and sunned, and rubbed down with pumice stone. Another coat of the linseed-oil varnish with pyroxylene is applied, baked, sunned and rubbed. Coloring matter is usually added to the varnish, and sometimes several coats are applied.

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VEGETABLE TANNING MATERIALS

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In the time that our tanners had the virgin forest to depend upon, hemlock and oak bark were the only vegetable tanning materials in use in this country, and they yet remain the source of greatest supply of tannin.

Hemlock Bark. The yearly cut of hemlock bark is between 800,000 and 900,000 tons, and of oak bark from 300,000 to 400,000 tons. The yield of hemlock has decreased about one-third in the last ten years, while the yield of oak bark has remained nearly stationary.

Because of increased production of leather during this period and because of the decrease in the peel of hemlock bark, it has become necessary to seek other sources of tannin supply.

Chestnut Extract. The first development to meet these conditions was the making of chestnut-wood extract, which has now reached a very important stage, from 450,000 to 500,000 barrels being produced yearly. In addition, chestnut wood is being used at many Southern tanneries directly in the leaches. Tanners have found the liquors obtained by this method insufficient in strength for their purposes, so some of them have added evaporating plants to their leach houses to concentrate their liquors to a sufficient strength for their use.

A barrel of chestnut extract is practically equal to a ton or a cord of either oak or hemlock bark, and while the yield from various extract factories differs, generally a cord of wood (128 cu.ft.) yields a barrel of the 25 per cent tannin chestnut extract.

Quebracho Extract. Quebracho extract is made from quebracho wood, a product of the Rio de la Plata Valley in South America. This wood contains from 18 to 24 per cent tannin. The solid quebracho extract contains about 65 per cent tannin and is sold on this basis. The yield of extract is generally 1 ton of solid extract from about 3½ tons of the wood. One ton of the solid extract is considered equivalent to 9 tons of oak or hemlock bark. There is now being imported about 60,000 tons of this solid extract or its equivalent in wood. As there are two factories manufacturing liquid quebracho in this country, the equivalency of this quantity of quebracho is 540,000 tons of oak or hemlock bark.

The tariff on this product was formerly $\frac{1}{2}$ cent per pound, but it has been raised to $\frac{3}{4}$ cent per pound in the present tariff bill.

Mangrove Bark. Mangrove bark and mangrove extract are also imported in quantity. Mangrove grows on the low shores of salt waters everywhere in the tropics. Along the Gulf of Mexico, mangrove averages, when properly cured, about 30 per cent tannin; that from the East Coast of Africa about 40 per cent tannin. East Indian and Borneo mangrove bark contains 30 to 40 per cent. This product enters free of duty, so that no accurate data is obtainable as to the quantity imported, but this, no doubt, is more than 20,000 tons annually, equivalent to more than 60,000 tons of oak or hemlock bark.

In the East Indies are two factories making solid extract from this bark, which comes upon our market as mangrove cutch; the quantity being brought in is not large now, on account of the duty of $\frac{7}{8}$ cent per pound, which the present tariff has placed on this product. It formerly came in free.

Myrabolams. Myrabolams are the fruit of an Indian tree, the harvest ranging from 30,000 to 45,000 tons per year. The United States is taking from one-third to one-half the production. Myrabolams contains about 30 per cent tannin. What is now being used in the tanning trade in this country will represent at least 45,000 tons of oak or hemlock bark. It is in the duty-free list.

Valonia. Valonia, the cup of an acorn, obtained in Asia Minor and Greece, is being imported in quantity. It contains about 40 per cent tannin. The harvest is from 50,000 to 60,000 tons per year. What is being brought into this country is equivalent to about 40,000 tons of bark per year. It is not subject to duty.

Divi-Divi. Divi-divi, wattle bark, are other tanning materials, but they do not come into this country in any quantity.

Palmetto Extract. Palmetto extract and caniagre are not produced in sufficient quantities to be commercially considered. Sumac and gambier are imported in large quantities, but do not go into the same trade that uses our native barks and cannot be compared with them.

From the estimates given of what the various tanning materials in use here are equivalent to in bark, it is seen that in total 2,300,000 tons are represented, about one-third being imported materials. At a fair valuation, these materials cost the tanner about \$23,000,000, the importations being about \$7,000,000 per year.

Chemistry of Tannin. From a chemical point of view, tannins are divided into pyrogallol tannins, such as from chestnut wood, myrabolams and valonia; and catechol tannins, such as from quebracho, hemlock, mangrove and oak bark. But from the tanners' viewpoint, the color and characteristics of the leather made from these various materials is of more importance.

Arranging these materials as to their color, that is, from a light yellow

to a dark red, we have sumac, myrabolams, valonia, bleached quebracho, oak bark, natural quebracho, chestnut, West Indian mangrove, hemlock and East African mangrove.

It is important for a tanner of oak in order to match color if he uses chestnut, to use also quebracho, so that a duplication of the oak color be obtained. There are many combinations that can be arranged from these materials to duplicate the oak, hemlock or union colors so long established as standards in the sole-leather trade.

Color of Leather. The color of leather produced is not the only characteristic which the tanner has to consider in the use of tanning materials; some wish hard leathers, some soft. It is well established that sumac is not suitable for hard leather; it is used on sheep and other soft leather exclusively. Myrabolams is considered a soft tannage. Valonia and chestnut are considered hard tannages. Oak, hemlock, mangrove and quebracho are used on both hard and soft tannages. There seems good reason to believe that by proper manipulation soft leathers can be obtained from any of these materials.

Palmetto extract, which often contains as much as 12 per cent of ash from salts soluble in the extract, the extract containing about 20 per cent tannin, invariably makes soft leathers when used alone. Sulphited quebracho extracts, which contain a large per cent of ash, also make soft leathers, and it is well known that hemlock liquors treated with salt will tan sheepskins as soft as does sumac.

From this it is a fair conclusion that salts in tanning solutions have a tendency to soften the resulting leather.

In tanning pickled sheepskins, that is, skins cured in salt and sulphuric acid, unless the tanning solution is salted—that is, treated with salt—the skins plump and lose their value, becoming hard and tinny when tanned; therefore, salt neutralizes the action of the sulphuric acid on skins.

The tanners of the hardest sole leather use sulphuric acid as a plumping agent, and tan with hemlock, oak, mangrove, valonia, chestnut, myrabolams and quebracho in various mixtures and proportions. It follows that the character of leather as to softness or hardness is more dependent on the relation of plumping acids to soluble non-tannins than it is on the character of the tanning material used. The term soluble non-tannins includes not only soluble inorganic salts, but also the similar organic non-tannins natural to the tanning material. The character of the organic non-tannins vary both as to their ability to furnish plumping acids and non-plumping acids, and likewise as to their repression of plumping acid action on the skin.

It is quite true, as a rule, that the pyrogallol tannins do not give the hard leathers that the catechol tannins produce, yet this may not of itself be due to the character of the tannin, but may result from the fact that gallic acid and non-plumping acid is usually present in the tanning solutions made from these materials. The subject is a broad one and

needs much investigation, but sumacs and nutgalls of the pyrogallol series show the largest changes into gallic acid and give the softest leather, while valonia of the same series shows small changes into gallic acid and gives a firm leather. On the other hand, chestnut extract containing in its extracted form, gallic acid, is not subject to much further change into this acid, and gives a firm leather.

Palmetto is of the catechol series, but gives a soft leather, which, as I have noted before, may be due to the presence of excessive quantities of inorganic salts, yet all the rest of this series are used for heavy leather tannages.

The nature of the combination of hide with tannin is not fully understood at present, but the tanner has the experience of generations in the use of raw vegetable tanning materials. This knowledge seems to have brought the practical tanner to conclusions, and he has determined in his own mind what raw material he wants to use to produce a certain result. It lies with the chemist to determine the reactions between the different tannins, non-tannins and their relations to salts and acids before the final decision can be reached as to the weakness or strength of the rule-of-thumb methods now followed by the tanner in determining the kind of tanning material to be used.

XLII

GLUE AND GELATINE

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Glue. Glue is an organic substance of varying chemical constitution obtained upon drying the solution yielded by boiling with water properly prepared animal matter such as skins, bones, etc. Stout soups which gelatinize when cold represent very impure glue solutions. In commerce glue appears in a great variety of forms, in rectangular sheets or cakes (sheet or cake glues), in wide or narrow strips (ribbon and noodle glues), in broken flakes (flake or chip glues), and ground or granulated in all degrees of fineness (ground and powdered glues); it is sometimes colorless and transparent, sometimes opaque, and it occurs in all shades of white, yellow and brown.

Gelatine. Gelatine is made from certain kinds of bones and parts of the skin selected, washed and treated with especial care so that the resulting product is much cleaner and purer than glue. Being extracted at a lower temperature or with relatively little exposure to heat, less of the fluid disintegration products of the stock are formed, and the jellying power is therefore greater. Broadly speaking then, glue is impure gelatine. In fact some very light colored high test glues so closely resemble gelatine, that an investigation of the conditions of manufacture or the presence of certain chemicals, is the only practical way to differentiate between them.

The derivations of the terms glue (from the unused Latin verb *gluere*, to draw together) and gelatine (from the Latin *gelare*, to congeal, a word allied to the English chill, gelid, jelly), at once call to mind the principal properties of these substances, for glue is chiefly used as an adhesive, whereas gelatine is valued mainly according to its stiffening or jellying properties. Both are typical colloids, Graham having in fact formed this term from the Greek κολλα = glue; and they consequently exhibit the characteristic properties of this interesting class of substances, which, in marked contrast to crystalloids, do not crystallize, do not readily diffuse, and are impermeable to each other.

Colloidal Condition. Instead of referring to colloids as a "class of substances," it would perhaps be more correct to speak, as Graham does (Phil. Trans., 1861, p. 183), of the "colloidal condition of matter," for most substances may exist in either the colloidal or the crystalloidal state, depending upon the nature of the solvent (e.g., certain soaps) or upon the conditions governing their formation (e.g., gold, silicic acid). The ultimate particles of colloids are much smaller than what we would ordinarily term a physical subdivision, but rather larger than chemical molecules; consequently their reactions stand midway between the physical and the chemical changes of matter, as may be seen by considering the properties of glue.

Glue absorbs a considerable quantity of cold water and swells up, yielding a jelly which, upon the application of heat, melts to a viscous sticky solution that gelatinizes again upon cooling. When dried at medium temperatures, glue can be again redissolved and redried indefinitely; and it is therefore called a *reversible* colloid to distinguish it from other colloids which, when once dried, are insoluble (i.e., silicic acid). When superdried at about 130° C., however, both glue and gelatine become insoluble, their constituent particles having approached too close to be again separated by simple soaking.[1]

Diffusion. Glue solutions will not diffuse through colloidal membranes (i.e., parchment paper and bladder), and their jellies are impermeable to other colloids. The solutions are coagulated by alum, formaldehyde and tannin, and also by chromium salts upon exposure to light. But these precipitates cannot be considered in a strict sense as chemical compounds, because their composition varies greatly with the conditions of their formation. They are nevertheless of great technical importance, forming the basis of the tanning process, for the glue yielding substances are rendered insoluble in like manner.

Chemical Constitution. We know comparatively little of the chemical constitution of gelatine and still less of the more impure and further hydrolyzed glue. The essential constituents of gelatine are carbon, hydrogen, oxygen, and nitrogen (other elements such as sulphur, phosphorus, etc., being present in absorbed impurities) and its empirical formula according to Schutzenberger and Bourgeois is $C_{76}H_{124}N_{24}O_{29}$; but such a formula does not give any information of value. On the other hand a study of the cleavage products of gelatine gives some insight into its extreme complexity. Skraup and von Biehler (*Monatshefte für Chemie*, 1909, Vol. XXX, p. 476), find that upon hydrolysis with hydrochloric acid, gelatine yields the following substances all of which, from the previous work of Fischer, Levene and others, have been shown to be contained in it.

[1] F. Hofmeister considers this as a regeneration of collagen, which he regards as the anhydrid of gelatine (*Chem. Centralbl.*, 1879, p. 74).

Glycocoll	Aminoacetic acid	$CH_2(NH_2)\cdot COOH$
Lysine	Trimethylglycine	$OH\cdot (N(CH_3)_3\cdot CH_2\cdot COOH$
Alanine	Aminopropionic acid	$CH_3\cdot CH(NH_2)\cdot COOH$
Phenylalanine	Phenyl-α-aminopropionic acid	$C_6H_5\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Leucine	Aminonormalcaproic acid	$CH_3(CH_2)_3CH(NH_2)\cdot COOH$
Aspartic acid	Aminosuccinic acid	$COOH\cdot CH_2\cdot CH(NH_2)\cdot COOH$
Glutaminic acid	Aminonormalpyrotartaric acid	$COOH\cdot C_2H_4\cdot CH(NH_2)\cdot COOH$
Histidine		$C_6H_9N_3O_2$
Arginine		$C_6H_{14}N_4O_2$
Proline	α-pyrrolidinecarboxylic acid	
Oxyproline	oxy-α-pyrrolidinecarboxylic acid	

Some of these substances may result from the decomposition of more complex constituents; in any event it is not yet known just how they are combined.

Raw Materials

Commercial glue stock may be divided into four classes:

1. Skin or hide.
2. Bone.
3. Sinew.
4. Fish stock.

Hide Stock. Most hide stock is produced by tanners, and as leather is more valuable than glue, only waste pieces of hide reach the glue maker. The principal kinds of such stock are: "pieces," or heavy trimmings from dried salted or limed skins (yield 18 to 50 per cent of glue); "fleshings," representing the scrapings from the flesh side (yield 3 to 40 per cent of glue); "skivings," which are parings from the hair or grain side of the skin or hide. Very frequently the yield of grease from fleshings exceeds both in percentage and value that of the glue especially in the case of "machine fleshings" which are usually thinner than those taken off by hand.

Calf, cattle, goat, sheep, deer, pig and horse skins are valued about in the order given.

A great variety of other kinds of hide waste also finds its way into the glue pot, as for example: *rabbit skin or coney stock,* a refuse produced by hatters who pluck off the fur for the manufacture of felt hats; *loom pickers,* representing discarded fragments of rawhide from textile machinery; worn-out Turkish rawhide moccasins, and many other kinds of rawhide and parchment waste. Tanned skin yields no glue although patents have been taken out for extracting the tanning materials and making glue from the skin thus made soluble.

"Dry stock" may have been either uncured or salted or limed before drying; "green" or wet stock may be "green salted" or "green limed."

Sinews. These come into the market fresh or green salted from the slaughter houses; they are also imported in dried state from South America, in which case they are frequently mixed with dried bulls' pizzles.

Bone. Quite a number of kinds of commercial glue stocks are produced from osseous tissue. The chief of these are enumerated below.

Green or Packer Bone. This consists of fresh sweet bone containing the marrow or bone fat and frequently adhering tendons. Such stock usually undergoes an immediate preliminary steaming at its place of production, by which the fat is separated and the keeping qualities of the bone so improved that it will stand transportation and storage. At the packing houses large quantities of fresh bone are produced in the canning departments. The long shin bones are sold to manufacturers of buttons, knife handles, etc. (whose refuse is later used), while heads, ribs, feet, etc., go direct to the glue factory. The hoofs and horns are usually first removed, for contrary to popular notion, they yield no glue at all. From cattle feet neatsfoot oil is rendered at a low temperature.

Country bone, which is chiefly butchers' offal and *junk bone* consisting of old dry bone from any source, are used mostly for the production of low grade glues.

Ossein. This is also called acidulated bone. It is prepared by leaching crushed bone in dilute (about 8 per cent) HCl, whereby the mineral constituents are dissolved, leaving a soft cartilaginous substance (collagen) which preserves the original shape of the fragment of bone. Before this process the bones are usually degreased in a closed steel tank with a volatile solvent (benzine or carbon tetrachloride) which is afterward distilled off from the grease and recovered. In the acidulation the main reactions are:

$$Ca_3(PO_4)_2+4HCl=2CaCl_2+CaH_4(PO_4)_2 \text{ (acid phosphate)},$$
$$Ca_3(PO_4)_2+6HCl=3CaCl_2+2H_3PO_4,$$
$$Ca_3(PO_4)_2+4H_3PO_4=3CaH_4(PO_4)_2.$$

From the acid solution the phosphoric acid is precipitated by the careful addition of milk of lime:

$$CaH_4(PO_4)_2+CaO=Ca_2H_2(PO_4)_2+H_2O,$$
$$2H_3(PO_4)_2+2CaO=Ca_2H_2(PO_4)_2+H_2O.^{1}$$

The "precipitated bone phosphate" as it is called, is largely used in the manufacture of "bone china"; and the "acid phosphate" is used in baking powders. In order to avoid an excess of lime, which would reproduce tricalcium phosphate, a filtered sample of the liquor is from time to time tested with molybdic acid solution, and the addition of lime stopped as soon as the failure of the ammonium phosphomolybdate precipitate to form, indicates that no more free phosphoric acid or acid phosphate is in solution. If an excess of lime be accidentally added, the error can be retrieved by the addition of a suitable quantity of the acid liquor. The

[1] In both the solution and precipitation of the bone phosphate other secondary reactions go on at the same time.

precipitate is pumped or forced by compressed air into a filter press and washed free from calcium chloride.

The soft collagen after washing out the residual acid (using lime water to neutralize if necessary) may be made directly into glue, but it usually is dried at a low temperature, yielding commercial ossein.

Dentelles. The ossein made from button makers' refuse is commercially known as " dentelles "; it is frequently called " spectacles " because of the fancied resemblance to eye glasses, of pieces from which the round buttons have been cut.

Prepared Horn Pith. This is an ossein stock made from the cornillons or interior supporting bony core of the horns. As it is the only part of the osseous structure that does not come in contact with flesh, horn pith yields a singularly pure and high class gelatine, and its porous structure renders easy its treatment and subsequent extraction.

Fish Stock. The heads, bones and skins of fish yield liquid glues which are not considered here. The swim-bladders of certain species of fish constitute what is known as isinglass.

Manufacture

The manufacturing operations at the glue factory are:

1. Preparing the stock;
2. Boiling the stock;
3. Treating and (4) drying the resulting glue solution.

Preparation. While the last two of these classes of operations are substantially the same for all stock, there are several methods of preparation, as might be expected from the great variety of raw materials.

Washing and Liming. Hide, sinew and ossein stocks after a brief preliminary soaking or washing in pure water to soften them and remove dirt, salt, etc., are placed in successive baths of lime water of gradually increasing strength, in which the stock swells up and becomes soft or " plump " so that it readily dissolves in the boiling kettle. The time required for liming varies with the stock and the season, always proceeding more rapidly in warm weather.[1] Thick dry hide pieces may take as long as six months to lime, whereas fleshings or thin skivings from hides limed at the tannery are frequently all ready to boil; coney stock, being very finely shredded, is usually boiled without liming. Practical experience is needed in this process, for an underlimed stock requires more time and heat to dissolve (thus injuriously affecting the quality of the glue), while overlimed stock is largely wasted in the washing process, which we will next consider.

The limed stock is taken from the lime pits (usually wooden vats sunk in the ground) and thrown into a washing machine, where it is thoroughly

[1] Hide pieces are often shredded or cut small to expedite the liming process, and the limes are sometimes " sharpened " with soda.

agitated in a continuous stream of water until practically all of the lime is washed out, which may be determined by cutting open a piece of stock and testing the interior with litmus or phenolphthalein. The slight remaining alkalinity is neutralized by soaking in very weak acid. For very clear glues HCl is used, the resulting calcium chloride being very soluble; H_2SO_4 gives a precipitate of $CaSO_4$ which renders the glue more or less opaque. At this point sulphurous acid is often used to bleach and further plump the stock; alum is also used to bleach the stock and harden the jelly. After thorough draining the stock is transferred to the boiling tank or kettle.

The "cone washer" is the one most in vogue in this country; the heavy wooden cone kneads, presses and turns the stock, effectively loosening the lime which is carried away by a stream of water entering from a perforated standpipe at the center and flowing through perforated iron plates at the sides or bottom of the tub.

Fresh Bone is sometimes boiled without even a preliminary washing; but if washed and degreased (so-called benzine process) it yields a much clearer glue. Bones may be made into glue by the "sulphurous acid process" patented by Grillo and Schroeder, according to which bones are disintegrated by moist sulphurous acid gas or liquid SO_2 according to the equation:

$$Ca_3(PO_4)_2+SO_2+H_2O=Ca_2H_2(PO_4)_2+CaSO_3.$$

Bones thus treated readily dissolve in the kettle; any acidity is neutralized with milk of lime, and the resulting "mud" after the calcium sulphite is oxidized by exposure to the air or by oxidizing agents, forms a valuable fertilizer.

The Boiling Process. In the extraction (or cooking) of glue the prepared stock is subjected to the solvent action of hot water by which the collagen undergoes a change into glue. Hofmeister regards this process as a hydrolysis proceeding in two stages according to the equations:

$$\underset{\text{Collagen}}{C_{102}H_{149}N_{31}O_{38}}\underset{+\text{ Water}}{+H_2O}=\underset{\text{Gelatine}}{C_{102}H_{151}N_{131}O_{39}};$$

$$\underset{\text{Gelatine}}{C_{102}H_{151}N_{31}O_{39}}\underset{+\text{ Water}}{+2H_2O}=\underset{\text{Semiglutin}}{C_{55}H_{85}N_{17}O_{22}}+\underset{\text{Hemicollin}}{C_{47}H_{70}N_{14}O_{19}};$$

but in dealing with substances of such variable composition, empirical formulæ of this kind have no great significance. Indeed the whole boiling process seems rather to be the gradual breaking down of colloid complexes with accompanying changes in the amount of absorbed water, and to consist of physical as well as chemical changes.

The higher the temperature and the longer the stock is exposed to it, the more rapidly these degenerative changes proceed and the lower the test of the glue. Hence it is desirable to extract the stock as quickly and at as low a temperature as possible. Here again the differences in

stock necessitate the use of different types of kettles or cookers, which may be grouped into two classes: 1. Open tanks; 2. Pressure tanks.

Open Tank. The open tank usually consists of a rectangular or round wooden tub having a closed steam coil over which a perforated false bottom of wood or iron is placed so as to leave a circulating space between the two. Upon the false bottom is spread a layer of excelsior to serve as a rough strainer, and on top of this the stock is thrown to within a foot or so of the top. Sufficient clear water is then added to cover the stock, and steam turned into the coil; when the desired temperature is reached, the steam is cut down to the minimum needed to maintain it until a sufficiently concentrated " soup " or glue solution is obtained, which may be determined by chilling a sample in a small cup. After skimming off the floating grease, this solution, the " first run " as it is called, is drawn off for further treatment, the stock again covered with water and a second run made in like manner, the same process continuing as long as any glue is left in the stock. The last run or washwater is extracted at boiling heat and is usually so weak that it must be added to another kettle, or be mixed with a stronger preceding run or else be evaporated.

Hide, sinew or ossein stocks are the ones usually boiled in the open kettle, and as they are greatly softened by their preliminary liming, they disssolve at comparatively low temperatures. As a rule three or four runs suffice to exhaust the stock, the residue of which (glue manure or tankage) is then dried for use as fertilizer. The tankage may contain much fat or insoluble lime salts of fatty acids, in which event it is first boiled with H_2SO_4 to liberate the grease.

Temperature. The temperature of boiling must in any event be above that favorable to bacterial growth, and usually begins at about 70° C. (158° F.), gradually increasing with each successive " run." The time required for boiling a " run " varies from one or two to six or eight hours, depending upon the softness of the stock and the temperature used. Several new types of open tanks have been patented in which the water is caused to circulate through the stock by mechanical means (rotary pumps, etc.), the object being to hasten solution; but with the ordinary tanks the stock is not disturbed or at most occasionally stirred with a long pole to open it up.

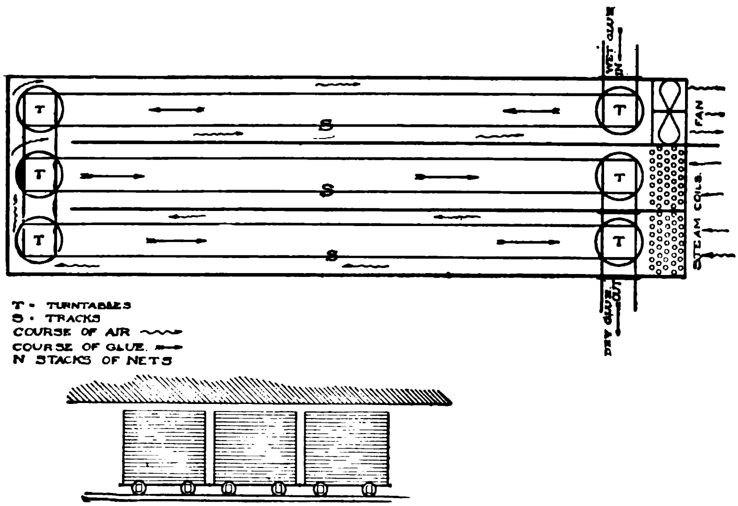
Pressure Tank. The pressure tank process of boiling glue is practically confined to untreated bones. The tanks consist of vertical steel or iron cylinders capable of withstanding several atmospheres pressure, having convex ends and large manholes at the top for filling and at the bottom for discharging the steamed bone.

The bones may be boiled with water under pressure (10–20 lbs.), the water may be allowed to trickle in from above while steam enters below (English process) or the condensation of the steam may supply the necessary water (French process). The successive runs of glue obtained are more concentrated than by the open tank method, but as a rule do not

have as strong a jelly; they are drawn off from time to time through a perforated false bottom. With fresh bones a large quantity of bone grease is incidentally produced.

Treating the Liquors. With ordinary glues, the liquors, concentrated in a vacuum evaporator if necessary, and preserved with antiseptics if desired, are run directly into galvanized iron pans or " coolers " where they set to a jelly, a process which frequently has to be assisted by artificial refrigeration if the boilings are weak or the weather warm. White or opaque glues are made by stirring in the desired quantity of oxide of zinc or other whitening material, before pouring the liquor into the pans.

Clarification. Although ossein and calf stocks generally yield very clear liquors, in order to secure the extremely clear jellies required for some glues and food gelatines, both chemical and mechanical treatment



Side view of one alley.

FIG. 339.—Ground Plan of Dry Room.

of the liquors are resorted to. The chemical methods consist in forming within the liquor a flocculent precipitate which tends to absorb and carry down with it the turbidity-producing particles. Alum, phosphoric acid or sulphurous acid followed by milk of lime, and blood or egg albumen are among the substances thus used. After the addition of albumen, to produce coagulation the liquor must be heated, which has an injurious effect on its jellying strength. The treated solution is filtered through a filter press or a pulp or bone char filter, and then run into the pans.

Drying. The " coolers " or moulds are dipped for an instant into hot water to loosen the jelly blocks, which, by means of sharpened stretched wires operated by hand or arranged in special glue cutters, are sliced into sheets of any desired size and thickness. These jelly sheets are spread upon galvanized or linen nets, and high piles of the

nets (called "stacks") are mounted upon wheeled trucks and are run into a dry room against a current of warm air which after passing over a large steam coil, enters the further end actuated by a circulating fan. Blower or pressure fans, and suction or exhaust fans are both used. See Fig. 339.

As the drying proceeds and the glue "skins over," it can be pushed nearer and nearer to the hot coil in front of which it gets its final "baking"; the stack is then withdrawn through a side door and the finished dry glue taken from the nets to be broken, ground, and packed into barrels, bags or packets.

Drying frequently causes the manufacturer much concern, for weak jellies are apt to soften and stick to the nets or even run entirely through to the floor; and besides the fresh jelly is open to the inroads of bacteria whose action may result in black or offensive smelling glue.

Grading and Testing

None of the so-called chemical tests for glue have any practical significance, but by experience it has been learned that glues made from certain stock and possessing certain physical characteristics give good results when used for certain purposes. The most important physical characteristics are the viscosity and the jelly strength of a solution of the glue, and in order to have some means of expressing these numerically, arbitrary standards have been selected which cover the wide range of commercial glues and gelatines. The following table gives the viscosity and jelly strength of such standards, determined on solutions of 25 grams of glue in 100 c.c. of water.[1]

Standard.	Viscosities (in secs.) at 80° C. solution 25-100.	Allowable variation of viscosities (in secs.).	Jelly strength (in ozs.) at 10° C.	Jelly strength (in gms.) at 10° C.
10	$15\frac{1}{2}$	$\pm\frac{1}{4}$	—	—
20	16	$\pm\frac{1}{4}$	—	—
30	$16\frac{1}{2}$	$\pm\frac{1}{4}$	—	—
40	17	$\pm\frac{1}{4}$	60	1701
50	18	$+\frac{1}{2}$	82	2324
60	19	$\pm\frac{1}{2}$	104	2948
70	20	$\pm\frac{1}{2}$	126	3572
80	21	$\pm\frac{1}{2}$	148	4196
90	22	$\pm\frac{4}{4}$	170	4820
100	23	$\pm\frac{3}{4}$	192	5443
110	24	$\pm\frac{3}{4}$	214	6067
120	25	± 1	236	6691
130	26	± 3	258	7314
140	28	± 5	—	—
150	34	± 8	—	—
160	40	± 12	—	—

[1] See *J. Soc. Chem.*, Vol. XXV. p. 158 (1906).

The standard viscosities were determined with a standardized pipette which permits the efflux of 45 c.c. of water 80° C., in exactly 15 seconds.

To determine standard jelly strength the "shot" test was found unreliable, and a special instrument was devised. It consists of a brass cylindrical vessel supported like a gas tank by four vertical rods, against which it slides with almost frictionless roller bearings. This brass cup is allowed to rest on a truncated cone of jelly of definite size, composition, and temperature; and shot are gradually poured into the cup until a definite compression of the jelly is observed. Beneath the cup are two vertical adjustable brass uprights 3.5 cm. high, connected with an electric bell circuit; so that when ths cup reaches their level, it completes the circuit and the bell rings.

The weight of the brass cup plus the weight of the added shot gives a figure which expresses the jelly strength.

The jellies are cast in brass cups 6 cm. high, 5.5 cm. in diameter at the open top, and 5 cm. at the bottom, which is closed with a tight fitting external friction cap. The jellies are removed by dipping the cups for an instant in hot water, taking care that no material loss results. The liberated truncated cones should be 4.5 cm. high, the cups being filled only to that level. They are placed in a thermostat until they reach the required temperature, 10° C.[1]

Thin blown glasses about 8–8.5 cm. high and 5.5 cm. in diameter are convenient for tests. 25 grams of each glue to be tested is broken into small pieces and soaked in 100 c.c. of water until softened; and at the same time a number of standard glues, above referred to, are treated in like manner. All the glasses are at the same time placed in a water-bath, heated to 80° C., and stirred until a perfect solution is obtained. More or less than 25 grams per 100 c.c. can be used as long as the standards and unknown glues are all treated alike. The reaction is determined with litmus paper. In cases where the degree of acidity or alkalinity is desired, a separate titration is made.

Viscosity or Running Test. Keeping the temperature uniform, the viscosity is determined by running the hot solution from a pipette, noting the time of efflux by a stop-watch. The relative viscosities are thus fixed in seconds. After each determination, the pipette is washed with hot water, and care must be taken that no partially evaporated glue or slime clogs the outlet. While running, the pipette may be kept in a specially constructed thermostat. More complicated viscosimeters, as Engler's or the Rideal-Slotte instrument, may, of course, be used.

The *odor* of the hot solution is then noted, and the glue rated as sweet or "off." Decomposition is readily detected, although it is often masked by phenol or ethereal oils. Besides, the smell gives some indication of the stock from which the glue was made.

[1] The standard jelly tester and pipette are to be had of Eimer & Amend, New York.

Grease. The glue solution is painted on a piece of white paper with a little aniline or dry color, and spots of " eyes " appear roughly proportionate to the amount of grease present.

Foam is determined by agitating the solution with a rod or mechanical agitator. An egg beater serves very well. Like grease, foam is estimated on a comparative basis.

Comparative Set. The glues are then taken from the bath, allowed to cool, and the comparative set or speed with which the jellies harden is noticed.

Jelly Strength or " Test." When the jellies have reached the room temperature, the jelly strength or " test " is determined. For speed and perhaps also accuracy, we prefer the " finger test," and grade the jellies comparatively by pressure with the finger tips, the unknown glues naturally grouping themselves as stronger or weaker in jelly than the several standards. Notwithstanding the personal equation, expert operators obtain much more uniform results in this way than are given by the various mechanical devices.

Melting-point. The melting-point of the jelly as described by R. Kissling (*Chem. Zeitung*, 1901, 25, 264) is also of considerable value, for generally speaking, it is proportionate to the jelly strength. It may be determined by the simple apparatus described by N. Chercheffsky (*Chem. Zeitung*, 1901, 25, 413).

Strictly speaking, a glue jelly has no absolute melting-point, for it softens up gradually and shows no sharp line of demarcation between solid and liquid. Perhaps the best way is to put the test glasses back into the water-bath, and gradually raise the temperature, noting comparatively how the jellies melt.

Absorption Test. Schattmann (*Dingler's Polyt. Journ.*, 1845, p. 115) proposed as a means of valuation, to determine the percentage of water a glue will absorb under fixed conditions. The water absorption is usually in proportion to the jelly strength, which is the more reliable figure.

Binding or Adhesive Strength. For this there is no one test that can have a general application; the glue must be tried under actual working conditions. It stands to reason that if a glue is to be used to hold clay to paper, it is of small interest what its binding strength is on mahogany, maple or porcelain blocks. Very often, in fact, a glue that will size paper perfectly will not make a joint.

Keeping Properties. The glasses are then allowed to stand uncovered at room temperature for several days to observe relative keeping qualities of the jellies. If the keeping property under special conditions is desired, these conditions are simulated.

As before suggested, these test figures must be read in the light of experience, and no one of them is sufficient to determine the value of a glue. The only test that can be accepted as conclusive is a practical trial of the glue under actual working conditions, which vary in each case.

Use. Glue is used for a multitude of purposes. Each line of work has its special requirements, and years of experience are necessary to pick out the right glue for the work. Trouble may be caused by a glue that is too strong as well as by one that is too weak. Although in using glue the most important thing is the selection of the right glue for the work, much depends upon its proper preparation and application. If anything that is glued up comes apart, the immediate verdict is " bad glue," which is often unjustifiable, for poor judgment or unskillful workmanship may be responsible.

In preparing glue for use the following points should be observed:

1. Use definite weights of glue and water. Glue is sold by the pound and should be used by the pound. 2. Soak the glue in cold water until it has thoroughly softened. Ground glue softens more quickly than sheet or flake glue, and is therefore preferable, other things being equal. 3. Melt in a water or steam bath, and keep at as low a temperature as is consistent with the work. Prolonged heating injures glue, so that it is advisable to heat up successive small lots of the soaked-up material, rather than have a large lot remain heated for a long time. 4. Make good evaporation from the glue-pot by the addition of water if necessary. 5. Use clean utensils. 6. Fit the strength of the solution to the work—don't use the glue too thick or too thin. 7. If surfaces are to be joined, have them dry and warm, if possible, and apply pressure until the glue has sufficiently " set."

Glues for particular purposes should be chosen as follows: [1]

Wood Joints. Most preferable are hide glues from grade 70 up. Lower test hide glues may give trouble. While some bone glues answer admirably, in general they should be avoided. The pieces to be joined should be thoroughly fitted, dry, and of seasoned wood.

Veneers. Most advantageous is a bone and hide, or bone and sinew mixture, testing between grades 50 and 70. Higher test glues are apt to set too quickly. Pure hide or sinew glue is better, but more expensive, while, for cheap large surface work, bone glue may be used. If worked on a veneering machine, freedom from foam is essential.

Sizing. As most sizing is done with special machinery, each case must be considered individually. Generally a free flowing glue, free from foam, is required. If used to surface paper, grease is undesirable, as is any marked acidity or alkalinity which might turn the shade of the colors with which the size is mixed.

Paper Boxes. For " setting up," quick setting hide glues, grades 70 to 90 are best. For " covering," lower test is necessary to prevent the glue setting too quickly; bone glues, testing grades 40 to 60, are most desirable. Of course, to the relatively higher test glues more water can

[1] These numbers refer to the standard grades given in column one of the table on page 826.

can be added; consequently they go further, and it is only a matter of proportion between strength and cost to determine the value.

Leather Goods and Belting. Here the main points are flexibility, tenacity, and resistance to moisture. Nothing under grade 100 should be used, and higher test goods are to be recommended, because they are less sensible to moisture, and interpose less mass between the surfaces joined. Fish glue, once largely used, is in disfavor, being too hygroscopic. Most leather belt manufacturers make their own special "cement," using high grade glue or gelatine as a base, and mixing it with glycerin and other ingredients.

Bookbinding. For rounding and backing, hide glues testing between grades 80 and 100 serve very well. If brittle low test or bone glues are used, the books are apt to crack down the back. Where simple pasting work is to be done, any sweet low-grade glue will anwer.

In all cases especial machinery demands glue suited to its particular requirements.

Gelatine. Only high testing sweet glues made from selected clean stock under sanitary conditions, and free from objectionable chemicals, should be sold as gelatine to be used for food purposes. Gelatine is a very valuable addition to the dietary as the use of calf's foot jelly for invalids would indicate, for it facilitates digestion and conserves the body's nitrogen. Being a typical reversible colloid, it is used in small quantity in marsh-mallow confectionery to prevent the crystallization of the sugar; and in ice cream besides preventing grainy crystallization, it inhibits the curding of the casein (an irreversible colloid) thus enhancing the digestibility of both the casein and milk fat. It has in fact been recommended as an addition to infants' milk.[1]

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An extensive bibliography of glue and gelatine by Dr. Rudolph Ditmar, including more than 150 references, was published in the *Zeitschrift für Chemie und Industrie der Kolloide*, Vol. I, p. 80 (1906).

[1] See *Zeitschrift für Chemie und Industrie der Kolloide*, Vol. V, p. 101 (1909); also *Jour. Am. Med. Assoc.*, Vol. LV, p. 1196 (1910).

Regarding certain technical uses of glue and gelatine, see "Colloid Chemistry and Some of its Technical Aspects," *Journal Soc. Chem. Ind.*, Vol. XXVIII, p. 280 (1909).

XLIII

CASEIN

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CASEIN belongs to that great family of nitrogenous organic compounds called proteins. It is a very complex colloidal substance found in the milk of mammals and in the juices and seeds of certain leguminous plants. In the modified form of cheese, casein from cows' milk has been used as a food from the earliest times, but its chemical composition and its manifold uses in the technical world were not known till recent years.

Casein exists in milk in the form of a colloidal suspension or emulsion, not in the free state but in combination with calcium. Hammarsten, who first investigated this substance, called it calcium caseinogenate. He used the name caseinogen for the protein complex as it existed naturally in milk and casein for the precipitated or coagulated substance. The calcium caseinogenate envelops the butter-fat globule and together with the calcium phosphate emulsifies it.

The casein molecule consists of six elements, carbon, 52.96 per cent; hydrogen, 7.04 per cent; nitrogen, 15.6 per cent; oxygen, 22.78 per cent; sulphur, 0.8 per cent; phosphorus, 0.82 per cent. Hammarsten gives the following formula for casein: viz., $C_{172}H_{274}N_{44}SPO_{55}$. The inner grouping of these atoms is still unknown.

Chemistry. Casein can be precipitated from milk or other solutions by the addition of very dilute acids in slight excess. This is the only method of obtaining it in the free state. There are certain other precipitants, but in this case the casein is obtained in a modified form, either in combination with the precipitant or as the original calcium caseinogenate. Solutions of the salts of the heavy metals precipitate the corresponding salt of casein with that metal. Saturation with neutral salts or alcohol gives a precipitate of calcium caseinogenate, while alkaloids, or anilin dyestuffs form complex compounds. These precipitants are not used except in cases where that particular compound is desired as the end product. Certain enzymes precipitate casein from milk, but the product is still further modified, often with a partial cleavage of the protein molecule.

The addition of dilute acids decompose the calcium caseinogenate with the formation of the calcium salt of the acid and the precipitation of free casein. There is considerable evidence, however, that the casein salt of the acid is first formed and then this is broken down into free casein by the water present. The action of enzymes is more complicated. Rennet precipitates cheese, which is not free casein but the calcium salt of a cleavage product of the casein molecule called paracasein. This enzyme is obtained chiefly from the gastric mucosa of calves. It will not act except in the presence of soluble lime salts, which ordinarily occur in sufficient quantities in milk. The action of rennet takes place in two stages; first, the enzyme splits the casein molecule into two parts, soluble casein and whey protein; then the calcium from the calcium salts in solution unites with the soluble casein and forms an insoluble curd of calcium paracaseate, while the whey protein goes into solution.

Casein is readily soluble in dilute aqueous solutions of the caustic alkalis, the normal and acid carbonates of the alkalis and alkaline earths, and in moderately strong acids. It is very easily broken down into simpler compounds (hydrolysis) if the above solvents are used in excess.

It is practically insoluble in alcohol, ether and water.

Casein is at least a tetrabasic acid, but like nearly all other compounds which contain the amino group, it can act also as a base. Consequently it forms salts with both acids and bases. The salts with the alkali bases can be obtained as dry powders by the evaporation of their solutions. The following salts of casein with bases have been prepared: Ca, Na, K, NH_4, Cu, Fe, Mg, and Hg. All soluble salts of casein can be rendered insoluble by treatment with formaldehyde, with soluble chromates, or with hexamethylenetetramine. In the dry or moist condition free casein is very susceptible to high temperatures. Its solutions are not coagulable by heat, are lævorotatory to polarized light and can be boiled without alteration.

Occurrence. Casein exists in cows' milk to the extent of about $3\frac{1}{2}$ per cent and forms 80 per cent of the entire protein content. Commercial casein is prepared exclusively from cows' milk. Ordinarily it is a perfectly white, ashless, hygroscopic powder, but under certain conditions it can be made in the form of glassy transparent grains.

Preparation of Technical Casein. One of the principal requirements of technical casein is freedom from fats. To this end sweet milk is put through a certrifugal cream separator and then 4–6 per cent caustic soda (or better 10 per cent sodium bicarbonate) is added. The amount of alkali is based upon the casein content of the milk. The solution is slightly warmed and put through the separator several times again. This procedure removes practically all the fats. The milk is run into a vat and dilute sulphuric or hydrochloric acid is added by degrees and the solution constantly stirred. Small portions are taken out from time to time and tested with acid until precipitation is complete. After precipi-

tation the curd is allowed to settle and the supernatant liquid siphoned off. The curd is stirred up with cold water, allowed to settle again and the water siphoned off as before. This is repeated until the effluent water is perfectly neutral.

The curd is then placed on cheesecloth filters, or on a sloping table and allowed to drain. Next it is put into strong cloths and pressed in an ordinary cheese press until no more water comes away. The curd must then be dried, and in order to facilitate this process, it is necessary

Fig. 340.—Vacuum Dryer.[1]

to break it up into very small pieces. This is done by a curd mill in which the curd passes between toothed rollers. Since casein is very susceptible to heat it must be dried at a very low temperature. This is accomplished in several ways. One of the best methods is by means of the vacuum dryer, which consists of a steam jacketed outside cylinder and a concentric revolving inside drum, heated by live or exhaust steam (Fig. 340). To the inside drum stirring blades are attached. The casein is dried between the inside drum and the outside cylinder, and is kept in constant motion by the stirring blades. After charging the apparatus, the manhole

[1] J. P. Devine, Buffalo, N. Y.

is closed and a high vacuum produced by means of an air pump, the vapors passing into a condenser.

Another vacuum dryer consists of a steel vacuum chamber with rubber shod doors. The requisite temperature is obtained by means of a coil of pipe filled with hot water or steam and placed around the inside of the chamber. The well pressed casein is placed on trays made by stretching cheesecloth over wooden frames. These trays fit into grooves on the inside of the vacuum chamber.

In some factories the fine curd is dried by feeding it into a revolving steel drum which is enclosed in another stationary one. The space between the two drums is filled with hot water. The entire apparatus is set on an incline so that the curd which is fed in at the upper end will pass through the drum as it revolves, and finally emerge in a well-dried condition at the lower end. After being placed in sacks or barrels the dried casein is ready for shipment.

Well-dried casein will keep indefinitely if properly protected from moisture. Since some of the bacteria of the milk must inevitably find their way into the casein, or outside bacteria contaminate it, the least amount of moisture will start decomposition. Some manufacturers sprinkle a few cubic centimeters of alcohol into each container. The alcohol vaporizes gradually and inhibits the growth of bacteria.

Technical Applications of Casein. The colloidal nature of casein renders it especially useful as an adhesive. The true solutions of casein are not colloidal, and consequently are neither viscous nor adhesive. To attain this end the amount of alkali used must not be quite sufficient to dissolve the casein, i.e., to make a true solution. In this case the casein is not all dissociated, but the entire mass is rendered extremely colloidal. The adhesive qualities can be imparted to casein solutions by the addition of tannin, or some alkali tannate, e.g., calcium tannate. The use of tannin, however, is not satisfactory, because of the discoloration produced in the solution by the action of tannin on the iron salts, which are always present to a very small amount, either in the casein or in the water used.

Preparation and Applications. Dried casein is soaked in an equal weight of water for two hours. The casein swells up but does not dissolve. At the end of that time 14 per cent borax in a hot saturated solution is added and stirred continuously till solution is complete. A thick mucilaginous dough results which can be thinned down to any desired consistency with hot water. Sodium bicarbonate, sodium tungstate, ammonia or the caustic alkalis can be used in place of borax. Sodium silicate and lime are best when a cement for porcelain, metals or stoneware is desired. Calcined magnesia produces a quick hardening cement. The adhesive properties can be increased by the addition of a little sodium arsenate, and a small amount of camphor will effectually protect all these adhesives from the ravages of insects.

These glues are put on the market in two forms, first in a dissociated

condition ready for use, second, as a dry powder in which the requisite amount of casein and alkali are ready mixed. In the latter case it is only necessary to add hot water to the powder, stir till dissolved and then thin down to the desired consistency with hot water. In the woodworking and cardboard industries the casein glues are superior to the ordinary adhesives. They are inodorous and gradually harden and become insoluble. Bottle labels and the like when moistened with formaldehyde, dried and coated with casein will effectually resist moisture. If a putty is desired it is only necessary to add powdered lime and knead until a thick dough is secured. This hardens very quickly and serves all the purposes of putty.

Casein in the Paper Industry. The paper industry offers an ever-widening field for the use of casein. The utility of paper itself, and all substances made from it, or wood pulp, owe their increased utility to some of the peculiar qualities imparted to them through the medium of casein solutions. Cardboard, paper flasks, buckets, bags and wrapping papers can be made waterproof by impregnating them with casein solution and subsequently exposing them to formaldehyde vapors. Paper bottles can be made sterile and impervious to moisture, milk, oils and other liquids by the same process. Wall paper can be made washable and antiseptic. Paper slates and drawing papers can be made erasable by coating them with casein solution to which finely divided magnesia or lime has been added. The sizing or enameling of paper in this manner has reached remarkable proportions. In this industry casein glue is used as a bind for the enameling substance and as a fixing agent for the colors.

Preparation and Application. Borax or soda casein is diluted down to the right consistency with hot water and finely powdered china clay, kaolin or chalk together with the desired coloring matter is added. This mixture is thoroughly incorporated together and placed in a vat. The paper to be coated is made to pass in an endless chain so that a small amount of this prepared mixture is transferred to the paper by a fine brush. The sheet then passes between other brushes which scrub the coating into the interstices of the paper and at the same time remove any excess. Next the paper passes through a drying chamber, where it is partially dried, and at last between heated rollers, which press the coating into a hard smooth finish.

Casein Paints. Casein combines with certain substances to form agglutinant compounds which are very stable and extremely resistant to moisture and other atmospheric changes. They all become more or less insoluble on exposure to air. In addition it forms compounds with coloring pigments, aniline dyestuffs and certain substances used for substrates. These properties render a solution of casein mixed with coloring matters especially useful as a paint or varnish, in which case the alkali solution of casein takes the place of linseed oil. Both acid and basic anilin dyes can be precipitated on any substratum by casein. Paintings

executed on canvas with casein colors will resist atmospheric changes for years. They show remarkable brightness of color and a splendid velvety sheen. They can be rendered waterproof by formaldehyde and are easily cleaned.

These paints are generally used as a thin liquid or paste in which the casein exists in a partially dissociated condition. They are similar to water-color paints in that they dry very quickly and without gloss. The surfaces to be painted do not need any especial preparation, although all previous applications of oil paints must be removed.

Preparation and Application. Casein paints consist of an alkaline solution of casein together with a suitable filler and color pigment. The binding medium is made by dissolving casein in an aqueous solution of caustic soda, borax, sodium bicarbonate, ammonia or sodium silicate. A small amount of an aqueous solution of soap, wax or rosin is sometimes added in order to protect the fine particles of coloring matters from atmospheric influences, and a few cubic centimeters of formaldehyde or phenol to render the casein antiseptic and to prevent the growth of molds and bacteria. For frescoing and inside ornamental work kaolin, china clay, lime or powdered feldspar is added as a filler and to give bulk and covering power. For artists' canvas the dissociated casein is emulsified by oils or fats so that the natural color of the pigment will not be altered by the binding medium. The addition of glass fluxes and metallic oxides produce an enamel-like finish and asbestos or diatomaceous earth gives a fireproof covering. For outside work on buildings, etc., the media must be incorporated with quicklime or cement both of which form insoluble compounds with casein upon drying.

The next step is to mix one of the above media with the desired pigments. It is absolutely necessary that the pigment be indifferent to the alkali used. The pigments most suitable for white are: baryta, white lead, china clay, lithophone or zinc white; for red, carmine, Indian red, and vermilion; for yellow, cadmium yellow, Naples yellow, or yellow ocher; for black, ivory black, or lamp black; for blue, cobalt blue, indigo or ultramarine; for green, chrome green, cobalt green or emerald green.

The proportions of binding medium, filler and pigment vary according to the nature of the work. When these paints are intended for shipment and use at a distance the above ingredients, in a dry condition, are mixed together in the proper proportions, ground to a fine powder in a paint mill and packed in tight containers. This mixture will keep indefinitely if protected from air and moisture. It is made ready for use by adding 50 parts of water to every 100 parts of the powder and allowing it to stand for some time. The alkali dissolves in the water and in turn acts as a solvent for casein. The mixture is then thoroughly incorporated together by repeated stirring and thinned down to the required consistency with hot water. The paint is then ready for use and can be applied in the same way as oil paints, the only necessary precaution being to keep the mixture

thoroughly stirred. These paints will adhere to almost any surface and will set very hard in a short time.

Plastic Masses from Casein. Casein is analogous to other compounds having strong adhesive qualities in that a great variety of plastic masses can be made from it, either alone in the form of a fine powder, or in an alkaline solution together with admixtures of other substances, such as paper, bone dust, powdered stone, etc. These mixtures possess the property of becoming very plastic under the influence of heat and in this condition they can be kneaded, rolled, pressed or moulded into any desired shape. They dry very quickly, are non-inflammable and do not shrink on drying provided an excess of water is avoided in the process of mixing. Any desired color can be added or transparent horny masses obtained. Articles made from these mixtures can be turned in a lathe, or shaped by any other cutting tool, and when finished take a fine polish.

Preparation and Application. If casein is used alone it is preferable to use the moist curd. This is heated to 175° F., and kneaded till a homogeneous mass is secured. It is then pressed or moulded into the desired shape and very carefully dried. If it is desired to incorporate other substances, the alkaline solutions of casein are preferable. In this case it is necessary to partially precipitate the casein with acids or salts in order to obtain the maximum plasticity. Other substances, such as powdered feldspar and pigments, are added and the mass treated as in the case of moist curd. Thin plates or ornamental designs of the above are used for paneling and inside decorations. For chessmen, toys, etc., the addition of strontium hydroxide and powdered marble give articles of exceptional hardness and durability.

In Germany great progress has been made in the manufacture of imitation celluloid articles from an admixture of casein and celluloid, or casein and cellulose or nitrocellulose. For this purpose casein and cellulose are dissolved separately in acetic acid and then mixed together and carefully evaporated. The inflammability of celluloid itself can be diminished by the incorporation of a small amount of casein with it.

The greatest achievement along this line, however, is *galalith*, a substance made from casein, either in an alkaline solution or in the dry powdered state. This is rendered colloidal by a small amount of acids or salts, and after kneading to a homogeneous mass and moulding, it is very carefully dried and rendered insoluble by formaldehyde. It is harder than celluloid, a non-conductor of electricity, inodorous and non-inflammable. It can be rolled into thin sheets or thick plates and used in place of mica on electrical instruments.

Other substances akin to the above, such as imitation leather or linoleum, can be made by impregnating a mass of vegetable fibers or animal hair with a mixture of oil, turpentine, glycerin and casein glue. This is partially dried and treated with aluminium acetate, after which it is thoroughly pressed between heated rollers. By pressing several sheets

together a leather of any desired thickness can be secured. A mixture of casein, vegetable oil, caoutchouc or rosin gives a substance which is one of the best electrical insulators known.

Uses of Casein in Dyeing and Printing Textile Fabrics. When textile fabrics are impregnated with a solution of casein, the fiber becomes coated with a thin layer of casein which materially increases the absorption of the dyestuffs in the bath. It thus acts as a mordant for the colors. When used alone it acts as a loading or softening agent for silk and cotton goods and renders the cloth more impervious to water. At first only the alkaline solutions of casein could be used, but recently it has been discovered that under certain conditions the dye bath could be made acid without precipitating the casein.

Preparation and Application. The general method consists in soaking the fabric in the casein solution and then passing it through the dye bath. Afterwards the fabric is dried and the coating rendered insoluble by exposure to the vapors of formaldehyde, or by dipping it into a solution of aluminium acetate. Another method is to incorporate the dyestuffs with the casein solutions and complete the operation of dyeing and mordanting in one bath. The addition of glycerin to the above solutions renders the fabric more flexible and increases the gloss. Finely divided coloring matters impart a metallic luster to the cloth, while soap increases its softness. After treatment with formaldehyde the tone of the colors remain as pure as those fixed with egg albumen.

A solution of casein in lime-water is used under the name of caseogum. Argentine is a compound of casein with zinc and gives a metallic luster to fibers, while glutin is a solution of casein in sodium tungstate.

Casein as a Food. From time immemorial casein in the modified form of cheese has been used as a food by humanity. Recently several new compounds of casein have been put on the market for this purpose, but the cost of production has prevented a wider use. Casein itself is somewhat indigestible, but several of its compounds with the alkalis are very soluble in water and consequently are readily acted upon by the digestive juices.

Preparation. The alkali salts of casein are made by the evaporation of their solutions and are put on the market in the form of dry powders. They are very nutritious and inodorous, and if kept dry will keep indefinitely. Several of them have different proportions of milk sugar and butter-fat added in order to increase their nutritive qualities. With the exception of cheese none of them are important as yet and consequently only a few are enumerated below.

Lactarine is one of the best known; it is a white powder composed of casein and a small per cent of mineral and non-nitrogenous matter. *Nutrose* is sodium caseate; *plasmon*, potassium caseate, and *eucasein*, ammonium caseate. *Sanatogen* is a compound of casein with sodium glycerophosphate. Synthetic milk is made from casein, sodium bicar-

bonate and a mixture of butter-fat and milk sugar. Flour and casein give a bread low in carbohydrates and find a use in certain dietary foods. A baking powder is on the market consisting of casein and calcium phosphate.

Casein in Medicine. The caseates of iodine, bromine, chlorine, mercury, iron, silver, arsenic, phosphorus and a large number of alkaloids and organic compounds are used in medicine to an ever increasing extent. The casein salicylates are said to be readily absorbed by the intestines and not to irritate the mucous membranes as do the other salicylates. When combined with alkaloids the casein residue seems to tone down the harmful effects of the drug without materially affecting the specific action desired. It is said that three times as much mercury can be administered in the form of the caseate to a dog or rabbit without causing death as can be given in the form of the sublimate.

Preparation and Application. The salts of the metals are made by treating an alkaline solution of casein with a solution of a salt of the metal. The halogen compounds are prepared by treating an alkali solution of casein with the gaseous halogen, or with an alcoholic solution of the same; while the compounds of casein with the alkaloids are made by treating a suspension of casein in alcohol with an alcoholic extract of the alkaloid.

Sodium caseate in a thick paste is used as an ointment. Mixed with a small amount of formaldehyde and applied to a cut or bruise it forms an elastic coating "*new skin*" over the injury and absolutely prevents outside infection by bacteria or other agency.

Sundry Uses for Casein. In addition to the foregoing there are other uses, which, though important, are not so extensively used. A few of the other industrial applications are as follows: in soap making, in priming artists' canvas, as a paint remover, shoe polish, photographic plates, roofing pulp, massage cream, artificial silk, and as an agent for solidifying mineral oil.

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